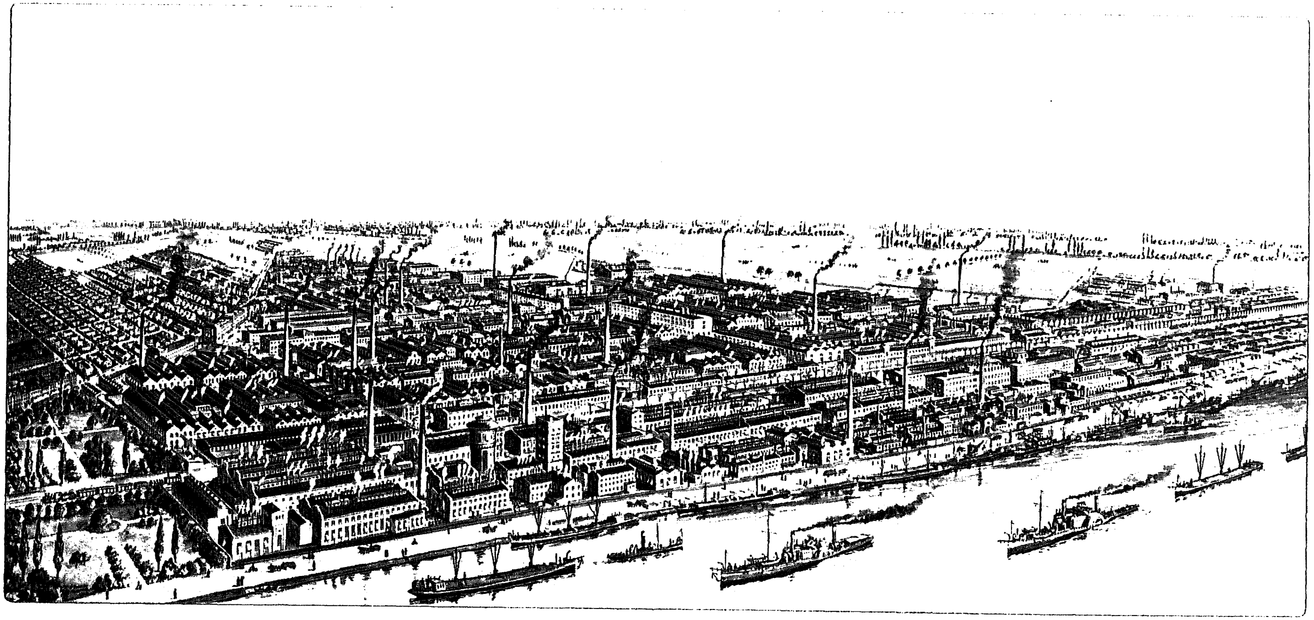
Badische

Anilin- & Soda-Fabrik

Ludwigshafen o/Rhine.

Indigo pure B. A. S. F.



BADISCHE ANILIN- & SODA-FABRIK LUDWIGSHAFEN o/RHINE.

CONTENTS.

Page

PREFACE 1

General Part.

I. Indigo 5

II. Indigo pure and Plant Indigo 7

III. Analysis of Indigo 10

Comparative Dyeing on Wool 11
Colorimetric Test 11
Survey of the Methods of Analysis 12
Titration with Hydrosulphite 14
Hydrosulphite Titration and Indigo Red 20
Titrimetrical Analysis by means of Potassium Permanganate 21
Effect of Indigo Red on the Titration with Permanganate 26
Gravimetric Analysis by the Vat Method 27
Control of the Reduction Method by Titration 30
Determination of Indigo on the Fibre by Extraction 32

IV. The Indigo Vat 34

Dyeing in the Vat 38

Part I.

Indigo pure B.A.S.F. and its Employment in the Dyeing of Cotton.

The Dyeing of Cotton and other Vegetable Fibres 49

1. General Remarks 49
2. The Dyeing of Yarn 50
3. The Dyeing of Warps 54
4. The Employment of Indigo pure B.A.S.F./*R* and Indigo pure B.A.S.F./*G* in dyeing Cotton Yarn 55
5. Special Methods of Preparation and After-treatment in dyeing Yarn 56
6. Indigo in Combination with other Dyestuffs 58

Page
7. Increasing the Fastness of Dyeings on Yarn 59
8. The Dyeing of Piece-goods 59
9. Special Processes for the Treatment of Piece-goods before and after Dyeing 66
10. The Dyeing of Cops and Cheeses 72
11. The Dyeing of loose Cotton and Sliver 75
12. The various Kinds of Vat employed for dyeing Cotton and other Vegetable Fibres 76
    a) Zinc-lime Vat 76
    b) Copperas Vat 79
    c) Hydrosulphite-soda Vat 84
    d) Bisulphite-zinc-soda Vat 91
    e) Bisulphite-zinc-lime Vat 93
    f) Hydrosulphite-ammonia Vat 93
    g) Fermentation Vats 95
13. Calculation of the Cost of an Indigo Dyeing on Cotton, Linen, etc. 100
14. Recovery of the Indigo removed in Washing and Souring ... 102
15. Linen, Linen and Cotton Unions, and Jute 105

Part II.

The Application of Indigo pure B.A.S.F. in Calico Printing.

INTRODUCTION 109
  Classification of the Processes used in Indigo Printing 112

I. Printing of Covering Pigments 115

II. Printing of Substances on the Undyed Fabric, which increase the Depth of Shade of the Printed Portions on dyeing in the Vat 118

III. Fixation of Indigo by Sublimation 120

IV. Direct Printing with Indigo 123
1. Development of the Process 123
2. The Glucose Process 126
    a) Development of the Process 126
    b) Directions for carrying out the Glucose Process 130
3. Printing of Indigo with Maltose 144
4. Printing of Indigo with other Carbohydrates 145
5. Printing of Indigo with Formaldehyde-sulphoxylate (Rongalite C patented) 146
    a) General Remarks 146
    b) Instructions for Printing 148
6. Printing of Indigo on Animal Fibres 150

Page

7. Printing of Indigo along with other Dyestuffs 151
8. Resists under Steam Indigo Blue 156
9. Printing of Indigo with simultaneous Discharge of Aniline and Alizarine Grounds 159
    - a) General Remarks 159
    - b) Indigo on Turkey Red 161
    - c) Discharge Printing on Paranitraniline Red and Alphanaphthylamine Claret 165

V. Indigo Discharge Printing 166

1. The Chemical Principles underlying the Discharge Process 166
2. Chromate Discharge 169
    - a) General Remarks 169
    - b) Instructions for Discharging with Chromates 175
3. Chlorate Discharge 183
    - a) General Remarks 183
    - b) Instructions for the Chlorate Discharge 187

VI. Resist Printing 190

1. Process of Resisting by Mechanical Means 190
    - a) Resisting by Tying, etc. 190
    - b) Battik Printing 192
    - c) Application of Mechanical Resists by Stencilling 195
2. Resists, which act both chemically and mechanically. The "Blue Print" 197
    - a) General Remarks 197
    - b) Instructions for Resist Printing 202

Part III.

The Application of Indigo pure B. A. S. F. in Wool Dyeing.

1. General Remarks 225
2. The Fermentation Vat 227
    - General Remarks 227
    - Plant for the Fermentation Vat 229
    - Suitable Indigo Brands for the Fermentation Vat 230
    - Vat Recipes 231
    - Working the Vat 235
    - Reactions in the Fermentation Vat 236
    - The Suint Vat 240
    - Indigo Solution B. A. S. F., Indigo Vat B. A. S. F. 60 %, and Indigo White B. A. S. F. /*E extra* for the Fermentation Vat 241
    - Indigo pure and Natural Indigo in the Fermentation Vat ... 242

Page
3. The Hydrosulphite Vats 244
    General Remarks 244
    Hydrosulphite-ammonia Vat 250
    Hydrosulphite-soda Vat 254
    Hydrosulphite-lime Vat 256
    Bisulphite-zinc-lime Vat 257
4. Indigo pure B. A. S. F./*R* 260
5. Treatment of Loose Wool 260
6. The Dyeing of Slubbing 263
7. The Dyeing of Woollen Yarn 265
8. The Dyeing of Piece-goods 267
9. Improvement of Defective Dyeings 270
10. The Tinting or "Blueing" of Wool in the Vat 272
11. The Dyeing of Unions 272
12. The Dyeing of Silk 273

INDEX 277

PREFACE.

Mankind takes, in general, a great pleasure in colour; the eye demands it as it demands light.

THIS remark, expressed by Goethe in his treatise on the æsthetic-ethical influence of colour, finds complete confirmation in the history of civilisation. In nature, colour is everywhere to be seen, and man, following consciously or unconsciously an artistic impulse, has striven from the very beginning to adorn himself and beautify his handiwork by means of colour decoration. Artistic comprehension and the range of technical possibility have changed with the centuries, but delight in colour was as much an attribute of our remotest ancestors as it is of modern man.

Of all known dyestuffs indigo is the oldest and at the same time the one which is still most used and in the most varied manner. Its study, therefore, is interesting not merely from a chemical standpoint, but it engages our attention also from the point of view of the historian.

However many-sided and various the employment of indigo is in different countries, yet it is used to-day much as it was at first: in the form of a vat. Modern science has not been able to make a change here and has produced nothing better than this chemical process, but it has taught and is teaching us that many of the traditional vat recipes, which are still used as of old, or with but little change, are too complex and unprofitable, and has replaced them by better and more rational methods. This, however, has not affected the principle of indigo dyeing.

When we consider the very great variety of the methods of applying indigo, a variety shown by no other dyestuff, no person at all competent to judge will expect to find each single case that occurs in practice mentioned and minutely described in a work like the present. This would be quite impossible. The purposes, the conditions, and the details of indigo dyeing are so very varied as to forbid it.

Nevertheless, the whole field, so far as it comes into practical consideration for dyeing and printing, is critically surveyed in this treatise, which purposes to give in a handy form all that the practical man need know. The expert is thus enabled to judge, on the one hand, which method of working is the most suitable for his special purposes, and further to learn what it is that takes place in the different operations, so that should failures occur he can himself ascertain the cause and apply the remedy.

General Part.

I.

INDIGO.

There is but little doubt that the art of dyeing blue by means of indigo, an art which can be traced back to the very oldest times, was first practised in India, the home of the indigo plant, and from here spread gradually to other countries. The oldest form of indigo vat was most probably a primitive fermentation vat; various forms of such vats are even now used in India and the East. Woad, which contains indigo, served for hundreds of years in Europe for dyeing blue, and trustworthy accounts of the Indian product were first brought back about the year 1300 by the Venetian Marco Polo from his journeys in the East, but not till 1516 did the first importation of indigo in any quantity into Europe take place. Then began a bitter struggle between the native woad and its Indian rival, which lasted more than two hundred years and was only brought to an end towards the close of the eighteenth century with the victory of the more valuable Indian dyestuff.

The methods of employing indigo have kept pace with the increase in our technical knowledge and have become in the course of time very varied, so that the dyestuff occupies now a not unimportant position in our civilisation. Besides the old fermentation vat, the dyer has now other forms of vats at his service, each with its own properties and most suitable for some special purpose. Modern dyeing technique, based on scientific principles as it is, has not been able to replace by any other the dyeing process peculiar to indigo, namely the vat. Owing to the character of the dyestuff it is not probable that this will ever be done,* so that the scientist confines himself to studying minutely the chemical processes of the different forms of vat in order to simplify the methods of working as much as possible and place them on a rational basis.

---

* Attempts made to employ "colloidal" indigo, which is soluble in water, for dyeing led to no useful result (Zeitschrift für angewandte Chemie, 1903, page 47).

II.

Indigo pure and Plant Indigo.

The *Badische Anilin- & Soda-Fabrik* first placed "Indigo pure B. A. S. F." on the market in July 1897, and in the thirteen years that have since elapsed synthetic indigo has taken its victorious course all over the world; a glance at the statistics suffices to show that in a comparatively short time natural indigo must be completely ousted. From the following tables can be seen how quickly the export of indigo from the German Customs District has increased, and, on the other hand, how the acreage and production of natural indigo in the two most important countries, British India and Java, have receded:

Export from the German Customs District.

1900	1 873	tons
1901	2 673	»
1902	5 284	»
1903	7 233	»
1904	8 730	»
1905	11 165	»
1906	12 733	»
1907	16 354	»

These figures refer to the actual weight of goods exported, the content of which, for the sake of comparison, can be taken on the average as 30 %.

The Export from British India

has dropped from about 6 758 tons in 1897/1898
to 1 500 » » 1905/1906

while the acreage planted (in Bengal, Madras, Agra and Oudh, Punjab)

has receded from 1 600 000 acres in 1896
to 283 900 » » 1908.

The Production of Java Indigo

was 12580 chests in 1898,
and is estimated at 2506 » for 1907.

This expansion of synthetic indigo has been assisted by its recognised advantages, *viz.,* regular composition and purity and an easy and simple method of application, and also by a reduction in price, consequent on improvements in manufacture, with which natural indigo has not been able to keep pace. The prejudice too, which at first induced many dyers to continue to use the old dyestuff, has disappeared, and nowadays no expert could be found who doubted the identity of artificial with natural indigo or the equal value of both products as regards fastness of the colour.

The opposition which characterised the absence of the substances which accompany plant indigo, such as indigo red, indigo brown, indigo gluten, as a disadvantage of Indigo pure is also silenced, and several years of practical experience have confirmed to the full the results of the experiments carried out as long ago as 1837 by *Schwartzenberg* and *Schwartz* (Bulletin de la Soc. ind. de Mulhouse, vol. X, page 413), and in 1899 by *J. E. Tulleken* (Bulletin van het Koloniaal Museum te Haarlem, No. 20).

The test of practical use has strengthened the conclusion reached by *J. Dépierre* (in his work "Teinture et Impression," Paris 1893, vol. III, page 233): "Of all the substances mentioned as contained in indigo, indigotine is the only one which is of value for dyeing." Some dyers, however, especially those in oriental and tropical countries and such as carry on the industry in their own homes in out-of-the-way places, prefer to adhere to the old traditions, and in order to meet these demands special brands have been prepared which closely resemble plant indigo in form and composition.

Besides this, indigo dyeing has been much enriched by the discovery of new derivatives of indigo. The brands Indigo pure B. A. S. F./*R* and Indigo pure B. A. S. F./*G* yield much redder and greener shades than Indigo pure and thus permit of a greater variety in the production of indigo dyeings. The methods of application of these new brands are the same as for ordinary indigo, and their properties as regards fastness are just as excellent — in some respects, indeed, even better.

The dyestuffs Indigo *RB* and *RBN* which we have recently brought into the market are interesting both on account of their practical value and their method of application. These products are derivatives of indigo, they are distinguished by the pure, full blue shades which they yield, and in respect of fastness are superior to indigo itself.

With the introduction of Indigo pure there followed a thoroughly scientific working out of the methods of application of this most widely used of all dyestuffs. Antiquated methods of vat dyeing, which up till then had been carried on, chiefly empirically, with plant indigo, were dispensed with and the dyer was enlightened as to the processes taking place and made familiar with economical, simplified methods. It is thus directly due to the introduction of synthetic indigo that vat dyeing has been rationally developed to the benefit of the consumer.

The natural product had to be taken by consumers just as it was, variations had to be accepted according to the result of the harvest or the district from which it came, and the customer had no technical advice as to the best methods of employment. Nowadays, on the contrary, he receives Indigo pure in the form most suited for his work and is informed as to the best process of application for his purposes, so that he can thus work more speedily and accurately.

III.

Analysis of Indigo.

Analysis of Indigo. General Remarks.

The question as to the value of an indigo has lost much of its importance for the consumer through the general use of the synthetic product. In the case of plant indigo, the usual estimates as to the percentage of indigo in a sample, made according to appearance and outward signs, were not at all trustworthy, and the purchaser could only obtain an accurate idea of the quality by a careful chemical analysis. In the case of Indigo pure the case is different: in whatever form or brand it is supplied, the content of dyestuff is always guaranteed as remaining constant.

We do not mean in the following pages to deal critically or at all exhaustively with the whole field of Indigo analysis* — to do so would take us too far —, but we intend rather to consider those processes which are actually of use in industrial practice both on account of the manner of conducting them and of their reliability. It is not, of course, to be expected that the methods applied to indigo should give the exact results of a mineral analysis, for the chemical reactions that take place are much too complex, and it must also be borne in mind that many differences arise owing to the difficulty of correctly obtaining samples. Plant indigo is brought on the market in the form of lumps and the quality is by no means the same even through one and the same lot. According, therefore, as samples are more or less correctly taken, the content may vary in the same parcel as much as 10 %; for this result the method cannot of course be held responsible. The only reliable method of taking samples is to grind the whole lot, mix well together and take a sample of the powder, but this can rarely be done.

---

* A careful, full compilation of the different methods, accompanied by complete references to the literature of the subject, is contained in the dissertation by *J. E. Tulleken*: "Indigo en zijn Onderzoek." (Leiden, J. M. N. Kapteijn, 1900.)

The procedure, therefore, is to take several small pieces from as large a number as possible of indigo lumps, grind these to powder and prepare for analysis a portion of the large general sample thus obtained.

Great care must also be exercised when taking samples of Indigo paste, *e.g.,* of Indigo pure pastes. They must be carefully stirred for at least 15 minutes before sampling. To prevent evaporation of the water the specimens must be kept in carefully closed vessels.

Before we describe those methods of analysis which come chiefly into practical consideration, we may mention shortly for the sake of completeness the method of

Comparative
Dyeing on Wool.

Comparative dyeing on wool,

and the

Colorimetric test.

The first method is not really an analysis, but only a rapid method of making a preliminary comparison of the various kinds of indigo. In many cases it is very useful. The results obtained are relative and do not tell the percentage composition of the dye, that is, they merely show whether one brand is better or worse than another. If the quality of the indigo used for comparison is known, we have thus a standard and can distinguish a good product from a poorer one.

The method consists in dissolving in sulphuric acid weighed quantities of the brands to be tested and dyeing the sulpho acids produced on equal quantities of woollen yarn or material. By comparing the dyeings, the strength of the sample of indigo in question can be gauged by the depth of the shade.

For refined and pure brands of indigo, the method is very good and reliable and is a valuable extension of the permanganate method described below.

In the case of crude products, however, the conditions are different. Besides indigotine, these contain other bodies in very varying quantities which also dissolve in sulphuric acid and can sometimes so influence the shade that a comparison, if not exactly impossible, is at least very difficult. On this account it is not correct to compare a pure indigo with a crude brand, or crude brands of very different kind with one another, *e.g.,* a fine Bengal indigo with ordinary Kurpah. The test can only be used to compare specimens of somewhat similar nature, if serious misconceptions are to be avoided. Special care is demanded in the case of certain Java brands which contain much indigo red. This latter when dissolved in sulphuric acid gives a red-violet colour on wool and makes the indigo appear much richer than its actual content of blue warrants.

Colorimetric Test of the Indigo Sulpho Acid.

The colorimetric test is closely related to the comparative dyeing. According to this method, the intensity of the solutions is compared in suitable apparatus and the colour content is determined from the result. The same limitations as to comparison of different shades must be made here as for the dye test, so that the method is only valuable under certain conditions.

Survey of the Methods of Analysis.

Survey of the Methods of Analysis.

If we leave out of consideration the method recently brought forward by *W. P. Bloxam* (Journal of the Chemical Society, 1905, page 975) by determining the nitrogen content, which has no practical interest, the spectroscopic method, which has a close affinity to the colorimetric test, and the sublimation method, we find that the processes for the examination of indigo can be divided into several sharply defined classes. Each group has its own special advantages which occasionally supplement one another and render certain processes most suitable for particular cases.

Titration with Reducing Agents.

1. Titration with reducing agents.

In this case the indigo is dissolved in sulphuric acid and then decolourised by a hydrosulphite of known strength. Very reliable results can be obtained if the instructions given are carefully observed.

The method described by *E. Knecht* (Journal of the Society of Dyers and Colourists, 1905, page 292) of titrating with chloride of titanium falls also under this group, but it has little practical interest and is not suitable for impure brands of indigo because the change of colour is too slight.

2. Titration with oxidising agents.

Titration with Oxidising Agents.

A solution of an oxidising agent, the effective strength of which is known, is added to a solution of indigo in sulphuric acid until all the colour is destroyed, and the amount of indigo present is then calculated from the quantity of standard solution required.

To this class belongs the simplest and, therefore, the most widely used analytical method, namely, by means of permanganate.

3. Gravimetric analysis by reduction (vat method).

Vat Method.

The indigo is first reduced to indigo white which is dissolved in alkali. The solution is then filtered and the indigo separated by blowing in air, the quantity being determined by weighing.

A very good and useful form of carrying out this, namely the hydrosulphite-lime process, has been published by *Rawson* (Chem. News, 1888, pages 7, 19, 29, 34).

4. Extraction methods.

Extraction Methods.

The sample is treated in a suitable apparatus with a solvent that dissolves only the indigotine, *e. g.,* boiling naphthalene, phenol, acetine, aniline, or glacial acetic acid. The amount of pure indigotine obtained from the extracting liquid is ascertained by weighing.

The best and most suitable solvent for indigo is glacial acetic acid, used either alone or with sulphuric acid. *Möhlau* and *Zimmermann* (Zeitschr. für Farben- und Textil-Chemie, 1903, pages 189 and 269) recommended a mixture of glacial acetic acid and sulphuric acid for the analysis of indigo as well as for its determination on the fibre. The process depends on the formation of indigo sulphate described by *Binz* and *Kufferath* (Liebigs Annalen, 325, page 200) from which the pure dyestuff is separated by diluting its solution in the acid mixture with alcohol.

Extraction with glacial acetic acid alone is very useful for determining the amount of indigo on the fibre.

Titration with Hydrosulphite.

Titration with Hydrosulphite.

This process, which has recently been much simplified by the use of hydrosulphite in powder, first put on the market by the *Badische Anilin- & Soda-Fabrik,* is to be recommended before all others, especially when the determination of impure indigo brands comes into question.

The hydrosulphite reduction method was first mentioned by *A. Müller* (Amer. Chemist, V, 128; more detailed in *Dépierre,* Teinture et Impression, vol. III, page 251; also *Bernthsen* and *Drews,* Berliner Berichte, 1880, page 2283). It gives reliable results, however, only when the conditions described below, which have been worked out by ourselves, are strictly adhered to.

From our researches we consider the hydrosulphite process to be best for titrating indigo for the following reasons:

1. It gives the most exact figures for the content of indigo blue, as the hydrosulphite is not influenced by the impurities in the indigo.
2. It is the quickest method (five to six hours) and requires the smallest amount of indigo (0·1 to 0·2 gr.).
3. The risk of error is reduced to a minimum owing to the change in colour being easy to recognise.

The hydrosulphite in powder mentioned above can be preserved almost without change in a dry, closed vessel, so that at any time a useful preparation for the simple production of a titrating liquid is at hand.

The hydrosulphite solution is standardised with the aid of a pure indigo of known content, the "normal indigo" or "working standard," and for the preparation of this in turn a chemically pure 100 °/o indigo, the "original standard," is necessary. The adjustment to pure indigo was formerly hindered by the difficulty of obtaining this product in any quantity. Now, since synthetic indigo of extreme purity is on the market in large quantities, this can readily be taken as "working standard" and the hydrosulphite regulated to it.

It was formerly a very difficult matter to procure a chemically pure indigo as "original standard," and all the samples used for preparing or standardising the solutions, such as refined indigo, indigo purissimum, and artificial indigo, were not perfectly pure, so that they gave more or less incorrect results.

It is, in fact, by no means easy to remove the last traces of impurity, but it can be done by starting with Indigo pure B. A. S. F. which is already very pure.

Several methods can be adopted for the

*Production of chemically pure Indigo.**

Chemically pure Indigo. Original Standard.

The purification by means of phenol, discovered by the *Badische Anilin- & Soda-Fabrik* (British Letters Patent No. 7593/03, German Patent No. 158500), is very simple, being based on the fact that hot phenol, when used in certain proportions, dissolves the impurities contained in indigo.

For example,

intimately mix one part of finely ground indigo pure with 5 parts of pure phenol containing 10% of water, and heat the mixture for several hours on an oil-bath, while stirring well, to 160—170° C. (352—370° F.) using a reflux condenser. When cold, filter on a hardened filter and wash well, first with pure phenol containing 10% of water and then several times with chemically pure, dilute caustic soda in order completely to remove the phenol. Finally, remove the caustic soda with distilled water, and dry the indigo at 105—110° C. (221—230° F.) till the weight remains constant.

Another method of procedure is as follows: Boil Indigo pure B. A. S. F. in powder several times with a 10% solution of chemically pure sulphuric acid, and finally wash well with hot water. Then refine it with hydrosulphite and caustic soda (1 part indigo, 8 parts caustic soda 42° Tw., $1^1/_2$ parts Hydrosulphite conc. B. A. S. F., and 10 parts water at a temperature of 40—45° C. (104—113° F.). Then filter the vat, pass air through it, filter off and wash the indigo, and then boil it successively with dilute, chemically pure hydrochloric acid and with alcohol. Then dry the dyestuff at 100° C. (212° F.) and crystallise it out from boiling glacial acetic acid. This is done by boiling the finely powdered indigo for about 10 minutes with glacial acetic acid and filtering as hot as possible. Filter off the crystals of indigo which separate out from the filtrate on cooling, wash them several times with alcohol and ether, and finally with hot, dilute, chemically pure hydrochloric acid. Then dry the crystals quickly at 105—110° C. (221—230° F.), and keep them in a well closed vessel. When filtering the pure crystals, it is best to use a so-called "hardened" filter, such as those supplied by the firm of *C. Schleicher & Schüll* of Düren, as, when using the ordinary filter paper, there is always a possibility of the crystals taking up small pieces of paper fibre as they are removed from the filter, thus rendering the indigo impure.

---

* *Möhlau* and *Zimmermann* (Zeitschrift für Farben- und Textil-Chemie, 1903, page 269) recommend the production of pure indigo by means of the monosulphate of indigo, whilst *Wangerin* and *Vorländer* (Zeitschrift für Farben- und Textil-Chemie, 1902, page 283) propose vatting a nearly pure indigo and washing it thoroughly.

Working Standard.

We assume that the indigo so obtained contains 100 % and by this "original standard" we determine the value of another purified indigo, for which for instance Indigo pure B.A.S.F. can be taken. With this sample, the so-called "working standard," all other brands of indigo to be tested are compared.

Preparation of the Solution of Hydrosulphite used for Titration.

Solution of Hydrosulphite for Titration.

Experience has shown that the colour reaction when titrating is more sharply defined the fresher the solution of hydrosulphite. On this account the quantity likely to be needed for each series of analyses is freshly prepared, even when the solution in stock is still quite capable of reaction. The hydrosulphite solution should be made slightly alkaline in order to preserve it longer, but 1 % caustic soda is to be considered a maximum, because the titration must take place in acid solution all through. To avoid a possible source of error, it is advisable not to make the solution too concentrated and to dilute it so that 40—45 ccm. of hydrosulphite solution correspond to 0·1 gr. indigotine.

Example:

Dissolve 3—4 gr. Hydrosulphite conc. B.A.S.F. in powder in 1 litre cold, distilled water to which 25 ccm. caustic soda of 42° Tw. have previously been added, and put the solution into the vessel marked *A* in figure 1 under coal gas. It is of no moment should a slight change occur in the hydrosulphite solution, for the solution must be titrated against the working standard for each analysis and the specimen to be examined tested immediately after this has been done.

Preparation of the Indigo Solution by Sulphonation.

Preparation of the Indigo Solution by Sulphonation.

This operation should be performed as follows. Grind the specimen of indigo to be tested to a fine powder in a mortar. Shake exactly 1 gr. of this powder into a small beaker containing 15 ccm. sulphuric acid 168° Tw. and make it carefully into as even a paste as possible by means of a glass rod which remains in the beaker during the sulphonation. Then rinse the edge of the beaker and the glass rod with another 15 ccm. sulphuric acid of 168° Tw. The sulphonation takes place in 2 3 hours at a temperature of 50—55° C. (122—131° F.), stirring once.

If this recipe is exactly followed, no difficulty will be experienced in completely dissolving the indigo without trouble by stirring, and besides this, decomposition of the indigo, which readily takes place at high temperatures, is altogether avoided. For measuring and preserving the acid we have found the graduated glass I shown in Fig. 1 to be suitable. When the solution of indigo in sulphuric acid has quite cooled down, pour it into cold water, cool once more to 15° C. (59° F.), dilute it to 1 litre in a graduated flask and then filter.

It is very important, when making up to a desired volume and filtering, to adhere to the foregoing order of operations and not, as usually given, first to filter the solution of the carmine which has been diluted with water and then make up the whole to 1 litre. In the first place, time is saved by working as directed above, for the troublesome washing of the filter is not necessary, and secondly it is a great advantage that the dirt is kept back by the filter, for by afterwards rinsing, the greater part is returned to the filtrate. By reason of the greater purity of the solution resulting from this simple artifice, the change of colour on titration can be recognised much more readily.

When dissolving the indigo in sulphuric acid, it is important to see that the temperature does not rise above that given, and that a stronger acid or too much acid is avoided, otherwise, especially at a higher temperature, partial destruction of the dyestuff may take place or darker solutions may be produced which make the titration difficult. In order to avoid errors, the brands of indigo which are to be compared must be sulphonated as far as possible under the same conditions. The standard indigo and the specimen to be examined must be treated with the same quantity of acid, at the same temperature, and for the same time.*

Standard Indigo Solution.

The **standard indigo solution,** containing 1 gr. indigo in 1 litre, is prepared by weighing out the corresponding quantity of the "working standard," *e. g.* 10·06 gr. of a 99·4 % indigo, sulphonating it as indicated above, pouring it into water and making it up to exactly 10 litres. The solution obtained in this way must be preserved in a bottle painted black, carefully closed and protected from light, and is used directly for comparing the samples to be analysed. It can be kept for several weeks without suffering change.

Method of carrying out the Titration.

Carrying out the Titration with Hydrosulphite.

The titration must be carried out in a stream of coal gas; in vacuo is better still, but this can be done only in very few cases. An arrangement of apparatus which has been found very convenient is shown in Fig. 1.

The bottle *A* contains the hydrosulphite solution, prepared as given above, which can be run into the burette by means of the pinchcock *Q*. Exactly 100 ccm. of the indigo solution are poured into a quarter litre Erlenmeyer flask. When working very accurately the air should previously be boiled out and the flask allowed to cool in a stream of coal gas, or the quantity of hydrosulphite solution corresponding to the oxygen in the water is determined and this quantity is afterwards deducted from the total amount of hydrosulphite used (*Wangerin* and *Vorländer's* proposal in the Zeitschrift für Farben- und Textil-Chemie, 1902, page 281). The means of closing the Erlenmeyer flask is shown in the sketch (Detail *b*).

---

* *Binz* and *Kufferath,* Färber-Zeitung, 1903, page 226.

The titration is effected by letting the hydrosulphite solution flow, at first in a fairly strong stream, through a tube *e*, which has a long, fine point, under the surface of the indigo solution to be titrated; at the same time the flask is shaken steadily. Towards the end of the titration the tube *e* is taken out of the indigo solution and the change in colour is brought about by adding the hydrosulphite solution drop by drop. The indigo solution changes from pure blue through bright green to yellow or brown, this latter marking the end of the titration. In contact with air, the blue colour returns. The liquid resulting varies in colour according to the purity of the indigo tested, a bright yellowish to brownish liquid being obtained.

For the sake of accuracy, it is advisable always to make two titrations to ensure that the titration has been correctly carried out. In the case of very impure brands of indigo, titrate three or four times in succession and strike the average of the results obtained. With a little practice, however, the results always agree.

The percentage of indigo in the sample is calculated as follows. Suppose for instance it has been found that

100	ccm.	of the indigo solution from chemically pure indigo (= 0·1 gr. indigotine, since there is 1 gr. "original standard" in 1 litre) require
42	»	hydrosulphite solution for decolourisation, and
100	»	of an indigo solution containing 1 gr. of the "working standard" per litre require
41·75	»	hydrosulphite solution,

then 42 : 41·75 = 0·1 : X, *i.e.*,

$$X = \frac{0 \cdot 1 \times 41 \cdot 75}{42} \text{ gr. indigo}$$

$$= 0 \cdot 0994 \text{ gr. indigo.}$$

That is to say, the "working standard" contains 99·4 % indigotine. If 1·006 gr. of this "working standard" are dissolved in 1 litre, a normal solution of indigo is obtained which contains 1 gr. indigo per litre.

If now

100 ccm. of the standard indigo solution (= 0·1 gr. indigotine)
42 » of a solution of hydrosulphite, and
100 » of a solution containing 1 gr. Bengal indigo per litre require
23·3 » hydrosulphite solution for decolourisation,

then $42 : 23{\cdot}3 = 0{\cdot}1 : X$

$$X = \frac{0{\cdot}1 \times 23{\cdot}3}{42} \text{ gr. indigotine}$$

$$= 0{\cdot}05548 \text{ gr. indigotine.}$$

Therefore the Bengal indigo contains 55·48 % indigotine.

It may be taken as a general rule that

if a ccm. hydrosulphite are necessary to decolourise
100 » of a 0·1 % indigo solution, and
b » hydrosulphite are required to decolourise
100 » of another sample of indigo, then

$$a : b = 0{\cdot}1 : X$$

$$X = \frac{0{\cdot}1 \times b}{a} \text{ gr. indigotine.}$$

Hydrosulphite Titration and Indigo Red.

Hydrosulphite Titration and Indigo Red.

Indigo red always accompanies indigotine in natural indigo. The quantity is from 2 to 4 % in the East Indian sorts, rising occasionally in the Java to 15 %. Since indigo red behaves on reduction as blue does under the conditions of the gravimetric vat analysis and on oxidation also is partly precipitated like blue, it is reckoned in when making use of this method. That is, the refined indigo produced from any raw indigo by refining in the usual way contains besides blue also the greater part of the red present in the initial material.

Indigo Blue along with Indigo Red.

If indigo blue is in solution along with indigo red, as for example in the solution of a Java indigo, the blue is first reduced by the hydrosulphite and then the red. Thus the hydrosulphite titration permits of the determination with a fair degree of exactness of indigo blue in the presence of red. The end of the

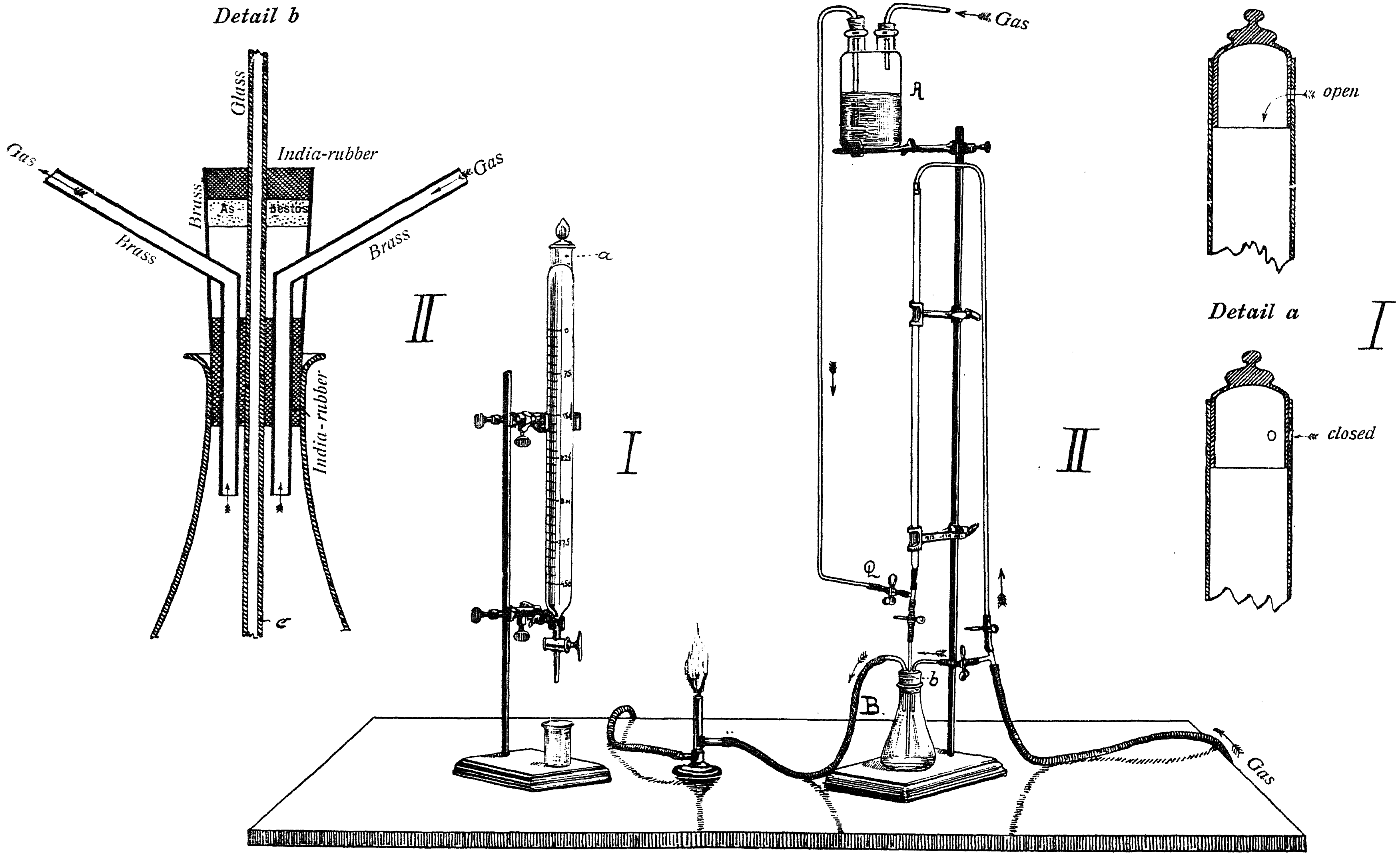


Fig. 1. Apparatus for the Titration of Indigo with Hydrosulphite.

titration for blue is recognisable by the change in colour from blue to violet. If blue is to be determined it should not be titrated for so long that the liquid appears pure red, otherwise wrong figures for indigo blue are obtained, but the hydrosulphite solution is added just until the liquid appears violet in reflected light and red in direct light. Then the figures in ccm. are read off for blue, the titration continued till the red has disappeared, when the figures are read off again. The difference between the two results corresponds to the indigo red present. The 0·1 % normal solution of the "working standard" of indigo is also employed as the standard of comparison for the determination of the indigo red, since indigo red and indigo blue have the same molecular weight.

Indigo red which has been decolourised by means of hydrosulphite can be oxidised again by the addition of a corresponding quantity of indigo blue solution, the solution turning red and indigo blue disappearing.

Examples:

Java indigo (1 gr. per litre) gave 65·4 % indigo blue, and
5·2 % indigo red.

Another Java indigo gave . . . 76·9 % indigo blue, and
6·6 % indigo red.

Titrimetrical Estimation by means of Potassium Permanganate.

Titration by means of Permanganate.

General Remarks.

By means of potassium permanganate a solution of indigo in sulphuric acid is oxidised to isatine and thereby decolourised; this method of titrating indigo was first recommended by *Mohr.*

The objection chiefly raised against this method is that not only the indigotine but also other organic bodies present in most kinds of natural indigo are oxidised by the permanganate and reckoned, therefore, as dyestuff. For this reason it is said that the results so obtained are too high and indeed that the greater the amount of impurity present accompanying the pure blue, *i. e.,* the more impure the indigo is, the higher will be the result.

This objection is not altogether unjust, but still it has been shown that by carefully working according to definite recipes the danger of oxidising beyond the indigotine is not so great as some have assumed. It has been proved experimentally that indigo red in very dilute solution is not attacked if proper precautions are taken and this is a point which is specially in its favour.

An unquestionable weakness of the method, on the other hand, is that in many cases the change of the blue to yellow which indicates the end of the titration cannot be detected with certainty, as towards the end of the reaction the yellow colour becomes more and more hidden by dirty brown and red impurities. With pure indigo the change in colour is from blue to green and then to light yellow; here the end of the reaction can be seen with absolute certainty. With the East Indian brands too (Bengal, Oudh, Kurpah, etc.), the end is also easy to determine in most cases, as the final colour is a more or less dark brownish yellow. When the indigo contains much red, as often is the case with Java indigo, the end of the reaction is uncertain, because the blue changes to a dark dull red-violet in the course of the oxidation. It is not so much with the poorer East Indian brands that too high results are obtained, but just with the Java, some of which contain large quantities of indigo, and this tends to show that they contain some impurity besides on which the permanganate reacts. *Rawson* drew attention as long ago as 1899 to the presence of a yellow body in Java indigo (Journal of the Soc. of Dyers and Colourists, 15, page 129).

No fixed rules can be given regarding the recognition of the end of the reaction, only experience and a practised eye can help to overcome this difficulty.

A great advantage of the permanganate method is the ease and quickness with which it can be carried out, enabling a practical man to examine a large number of samples in a short time with comparatively accurate results. It is very suitable and perfectly reliable for pure and refined sorts of indigo, presuming that the permanganate solution has been standardised against chemically pure indigo. With crude indigo the results are generally too high (by 0·2—3 %). It yields, however, approximate results, and at the same time by means of the colour changes gives an idea of the nature and quantity of the impurities present.

Taking everything into consideration, it may be said that the method is better than it is generally held to be.

By titrating impure indigo (especially plant indigo) with permanganate it is generally found, in comparison with the titration with hydrosulphite, that too high figures are obtained. This, however, is readily explained by the susceptibility of the permanganate and the presence of easily oxidisable substances in natural indigo.

Standardising the Solution.

Standardising the Solution for Permanganate Titration.

The foundation of the whole analysis depends on the correct determination of the oxidising power of the permanganate solution, *i. e.,* on the standardising of the solution.

In order to obtain a correct basis to work upon, it has been proposed to standardise the permanganate solution, on the one hand, with indigo and, on the other hand, with pure oxalic acid, and by this double relation to calculate the amount of indigo from the normal oxalic acid solution (*A. Classen* in Mohr's "Titrirmethode," 6th edition, 1886, pages 799, etc.).

This proposal depends upon the following theoretical equations:

$$4\,KMnO_4 + 5\,\underset{\text{(Indigo)}}{C_{16}H_{10}N_2O_2} + 6\,H_2SO_4 =$$

$$10\,\underset{\text{(Isatine)}}{C_8H_5NO_2} + 4\,MnSO_4 + 2\,K_2SO_4 + 6\,H_2O$$

and

$$2\,KMnO_4 + 5\,\underset{\text{(Oxalic acid)}}{C_2H_2O_4} + 3\,H_2SO_4 =$$

$$2\,MnSO_4 + K_2SO_4 + 10\,CO_2 + 8\,H_2O.$$

From these the following relations are arrived at:

63 oxalic acid ($C_2H_2O_4 + 2\,H_2O$) are equal to
31·6 potassium permanganate, equal to
65·5 indigotine; or

1 ccm. normal oxalic acid (63 gr. per litre) is equal to
1 » normal permanganate of potassium,* equal to
0·0655 gr. indigotine.

1 gr. oxalic acid is, therefore, theoretically equal to 1·03968 gr. indigotine.

Experiments, however, have shown that although these calculations may be theoretically correct they do not always represent the real state of affairs and can give rise to mistakes. Evidently the oxidation does not proceed quantitatively under all circumstances in accordance with the equations given, especially when other oxidisable substances are present along with the indigo.

The only correct method is to drop the comparison with oxalic acid altogether and to standardise the permanganate solution with pure indigo, *i. e.,* just as in titrating with hydrosulphite, to measure the indigo against indigo. It may be mentioned that *Mohr* first attempted this although in an imperfect manner.

The chemically pure indigo to be used as "original standard," the "working standard" and the normal indigo solution prepared from this are obtained as directed in the case of titration with hydrosulphite.

The sulphonation of the indigo is effected as described on page 17, observing the same precautions with regard to concentration and temperature.

To exclude the possibility of error due to the action of the permanganate on the sulphuric acid, which is not always equally pure, the same acid should always be used for preparing the standard solutions and dissolving the samples to be tested; for this reason it is advisable to keep a fair quantity of acid (say, a few pounds) in stock for constant use.

In order to obtain solutions of indigo of the greatest possible purity and clearness, *Grossmann* (Soc. of Chem. Industry, 1905, page 308) has proposed to precipitate the impurities from the dilute solution by the addition of pure calcium carbonate. This method is especially worthy of note for the analysis of impure brands.

---

* With reference to normal permanganate, *Mohr* says: "If we call a liquid normal with regard to oxidation when it contains 1 atom = 8 gr. available oxygen per litre and can give this off, then we have the following solutions: normal permanganate 31·62 gr. per litre; one-tenth normal 3·162 gr. per litre."

The solution of indigo is made more dilute than for titration with hydrosulphite, being diluted in about the proportion of 1 : 20 000. If a less dilute solution is taken, the amount of permanganate used varies; it remains constant with a more dilute solution.

A solution of 0·5 gr. of the purest permanganate in 1 litre water serves as titrating liquid. It is prepared by dissolving the salt at ordinary temperature, filling up to one litre, shaking well, and filtering through glass wool.

Method of Procedure.

Method of Procedure in the Permanganate Titration.

Sulphonate 1 gr. indigo as directed above, make it up with water exactly to 1 litre, and filter. Mix 50 ccm. of this solution of indigo with 1 litre distilled water in a porcelain dish, and, while stirring regularly, add the permanganate solution slowly from a burette to the solution. The blue colour disappears giving place to an olive. At this stage add permanganate very carefully, drop by drop, till the colour is a pure yellow to brownish yellow according to the purity of the indigo under examination. The last trace of green tinge must have disappeared. The change of colour is most readily detected by the eye when looking from above at that part of the liquid just at the edge of the vessel.

Examples:

1. Original standard 100 %.

50 ccm. = 0·05 gr. chemically pure dyestuff. Amount of permanganate used: 45·0 ccm. 1 ccm. = 0·00111 gr. indigo.

2. Working standard, pure indigo.

50 ccm. = 0·05 gr. of the product require 44·8 ccm. permanganate. 44·8 × 0·00111 = 0·04977 gr., *i. e.,* 0·1 gr. of this quality contain 0·09954 gr. chemically pure indigo, or, in other words, it contains 99·5 %. In preparing the standard solution from this, this percentage composition is used in the calculations.

3. Refined plant indigo.

50 ccm. = 0·05 gr. of the product require 42·9 ccm. permanganate. 42·9 × 0·00111 = 0·04766 gr., *i. e.*, 0·1 gr. contain 0·0953 gr. chemically pure indigo. The content is, therefore, 95·3 %.

4. Bengal indigo.

50 ccm. = 0·05 gr. of the product require 27·1 ccm. permanganate. 27·1 × 0·00111 = 0·030105 gr., *i. e.*, 0·1 gr. contain 0·0602 gr. chemically pure indigo. The content is, therefore, 60·2 %. The titration ends with a reddish brown yellow, but the disappearance of the greenish tint is easy to recognise.

5. Java indigo.

50 ccm. = 0·05 gr. of the product require 34·2 ccm. permanganate. 34·2 × 0·00111 = 0·037996 gr., *i. e.*, 0·1 gr. contain 0·07599 gr. The content is, therefore, 76 %. The titration ends with a dull dirty colour. The disappearance of the last trace of blue hidden by the olive tint cannot be recognised with certainty, so that the result is possibly too high.

Effect of Indigo Red on the Titration with Permanganate.

Effect of Indigo Red on the Titration with Permanganate.

In very dilute solution, as prescribed for analysis, indigo red is hardly attacked by the permanganate, so that this method permits of the determination of the blue in the presence of red with tolerable accuracy.

To check these conditions the following experiments were made. Pure indigo 99 % and pure indigo red, 2 gr. each, were dissolved with sulphuric acid and made up to 1 litre each as described above. The red was prepared by refining a Java indigo with a large red content and extracting the refined product with alcohol in such a way that in each case only the first fractions containing pure red were worked up (by evaporating) to red.

The blue solution was then mixed in definite proportions with the red and titrated with permanganate in the usual way. The permanganate was added until the green, bluish green, and bluish violet tints disappeared and gave place to an orange, or reddish brown to dark red-violet coloration. In all cases the addition was continued until the orange, or red, shade of the liquid predominated. By comparing the calculated percentage of indigo blue with that found by analysis, an idea of the reliability of the method could be formed.

Percentage of red added	Calculated percentage of blue	Percentage of blue found by analysis
2	97·02	96·8
4	95·04	95·3
8	91·08	91·6
10	89·1	89·4
12	87·12	87·2
15	84·15	84·1

A common Brazilian indigo that contained hardly any red was analysed by the permanganate method and was found to contain 38·7 °/₀ of blue; 8 °/₀ of red were then added and it was again analysed and found to contain 38·4 °/₀ of blue.

The figures agree sufficiently with each other to show that indigo red is not oxidised with the indigo blue and is not determined as such in an analysis with permanganate if the necessary precautions are observed.

Gravimetric Analysis by the Vat Method.

Gravimetric Analysis. General Remarks.

If it is considered to be of the first importance for the dyer to know how much indigo can be rendered serviceable for his purpose in the vat, then the reduction, or vat, method of analysis deserves preference before all others, for the chemical reactions made use of in estimating the blue are the same as those which come into play in the dyeing process, *viz.*, reduction of the indigo in an alkaline solution and oxidation by the air. From it, therefore, direct conclusions can be drawn as to what the result of the dyeing process should be.

In order to be able to criticise not only estimations of indigo, but also the whole subject of indigo dyeing, it is necessary to be perfectly clear as to a fact which, although of fundamental importance, is still not appreciated to the extent that its significance demands.

The amount of pure indigo which is present in the different kinds of vats (grape sugar, copperas, zinc, and hydrosulphite vats) and can be made use of, by no means corresponds to the amount of dyestuff that has been added to them, for according to the properties of the reducing agent a greater or less decomposition of the indigo blue takes place, which means a corresponding absolute loss.

This was first pointed out by *Ullgren*, who stated that whenever indigo is reduced, there is always a constant loss of 13 % reckoned on the amount of pure dyestuff (Annalen, 1865, vol. 136, page 96). The statement in this form is not correct, but the fundamental idea is quite right: a distinct unavoidable loss of dyestuff takes place in every kind of vat, even though worked under the most favourable conditions, and the extent of this loss depends on the action of the reagents employed upon one another, and upon the indigo. The hydrosulphite vat alone is an exception as it gives up its indigo again almost quantitatively.

For analytical purposes, therefore, as suggested by *Rawson* (Chemical News LI, page 255), only the hydrosulphite vat can be used, as practically no loss takes place if the work is carried out correctly. The alkali used is lime, as certain brands of indigo give solutions with caustic soda that cannot be filtered, and the lime has also the advantage of precipitating any indigo brown present.*

The method is not quite simple, especially if one wishes to work with a closed apparatus and in an atmosphere free from oxygen. Fortunately, indigo is not destroyed by a large excess of hydrosulphite, so that by reducing strongly the formation of a flurry on the vat which is being analysed can be almost entirely avoided. The large excess of hydrosulphite, which must here be much greater than that used in a dye vat, brings about complete solution and totally prevents a separation of the indigo.

---

* According to *Binz* and *Rung* (Zeitschrift für angewandte Chemie, 1899, page 516) indigo white does not form an insoluble combination with an excess of lime. Experiments have proved this statement to be correct.

This method, like all others that depend upon reduction, has the disadvantage that part of the red contained in the raw indigo is determined along with the blue. The indigo weighed does not contain 100 °/o of the pure dye, but is merely a well refined indigo, and the amount of chemically pure indigo it contains must be found by analysis with permanganate. A large number of experiments has shown that 95 °/o can be accepted with certainty as the amount of indigo obtained in this way, and calculations can be based on this. The remainder consists of indigo red, several undefined impurities, and a little ash. The Java indigos again form an exception, for the refined indigo obtained from them sometimes contains only 90 °/o or even less. In such cases the determination must always be checked by permanganate.

From the weight of this refined indigo, therefore, there must be deducted 5 °/o, or the amount of impurities shown to be present by permanganate (if a titration is made), and the remainder then reckoned as pure indigotine.

Method of Procedure.

Method of Procedure of the Gravimetric Analysis.

Mix 12—20 gr.	finely powdered indigo according to quality (on an average 15 gr.) in a flask that has been exactly weighed, with
200 ccm.	milk of lime 20 °/o and about
250 »	hot water. Then add
30 gr.	hydrosulphite conc. in powder and enough water at a temperature of 60° C. (140° F.) to make up to about 1 kilo.

Now warm the mixture to about 50° C. (122° F.) until the solution has become perfectly yellow, which requires about 2 hours. An occasional careful shaking helps the reduction, but for the last 15 minutes the flask should be allowed to stand quite still, so as to let the sediment settle. The flask is then exactly weighed and the clear solution is filtered with a filter

6622 N031 1805

pump; about 200 gr. of this filtrate are now weighed off, diluted with 1 litre water at 60° C. (140° F.), and a stream of air is passed through this for $1^{1}/_{2}$—2 hours till the indigo blue is completely separated. The indigo so obtained is now collected on a hardened filter, washed with hot, dilute, pure hydrochloric acid (30 ccm. hydrochloric acid per litre water), then washed again with water, dried, and weighed.

In making the calculation it must be taken into account that the whole of the liquor weighing 1 kil. was not a uniform solution of indigo, but also contained solid substances (lime and impurities). The solids thus weighed along with the solution are not indigo solution, and their weight must be subtracted in order to obtain the quantity of the pure solution corresponding to the amount of indigo used. If 30 gr., which is the average weight of these solids, are deducted from the total weight, the result will be almost exactly correct. The calculations are then made from the net weight so obtained.

Example:

15	gr.	Oudh indigo
250	ccm.	hot water
200	»	milk of lime 20 %
30	gr.	Hydrosulphite conc. B.A.S.F. powder
525	ccm.	water.

Net weight after warming for two hours	1004·5	gr.
Deducted for solid substances	30·0	»
Net weight of the liquor .	974·5	gr.
Amount of this taken . . .	201·3	»

and from this 1·830 gr. were obtained. Assuming a content of 95 % pure indigo, this corresponds to 1·738 gr. of indigo 100 %. The amount of indigotine contained in 974·5 gr. of the reduced liquor, corresponding to 15 gr. Oudh indigo, is therefore 8·41 gr., or, expressed as a percentage, 56·1 %.

Control of the Reduction Method by Titration.

Control of the Reduction Method by Titration.

In order to be quite certain of the results, a crude indigo should be examined by both the permanganate and the reduction methods. The latter is authoritative as it is based on the same reactions as those taking place in dyeing. The permanganate method of analysis is sufficient for pure indigo (refined indigos, Indigo pure).

The results of the two analyses generally agree fairly well with one another, but frequently the figure obtained by the permanganate method is a little higher. The following figures have been taken indiscriminately from a collection of the results of about one thousand analyses made according to both methods:

Indigo brand	Reduction analyses %	Permanganate analyses %
Java	80·1	80·9
»	72·3	75·0
»	70·5	70·4
»	77·2	77·0
»	70·8	71·9
Bengal	61·5	61·4
»	59·3	59·9
»	61·0	61·7
»	62·0	61·9
»	56·1	56·8
»	67·7	69·3
Oudh	49·0	49·0
»	52·1	52·8
Bimlipatam	49·6	50·3
Benares	58·9	59·2
Karachi	28·9	29·7
»	15·1	17·0
Mexican Indigo . . .	29·1	29·5

Determination of Indigo on the Fibre by Extraction.

Determination of Indigo on the Fibre.

Glacial acetic acid was first proposed as a solvent for indigo by *Lenz* (Zeitschrift für Analytische Chemie 26, 535) and has proved to be very suitable for the estimation of indigo on animal and vegetable fibres according to the method worked out by *Scheurer* and *Brylinski* (Bulletin de Mulhouse, 1898, pages 33, 192, 287, and *Binz* and *Rung* (Zeitschrift für angewandte Chemie, 1898, N° 39).

The process is simplest in the case of wool, as glacial acetic acid has very little action on the fibre and the figures obtained are sufficiently accurate for practical requirements, *e. g.*, for the calculation of the amount of indigo required for a given shade.* The best method of procedure is as follows:

About 25 gr. of wool dyed with indigo are extracted with boiling glacial acetic acid in a Soxhlet apparatus until the whole of the indigo is removed. The extraction must be completed without interruption, otherwise the indigo crystallises out on the wool and is very difficult to bring into solution again. Dark shades require about twelve hours to bring about complete removal of the indigo. The solution thus obtained, from which the greater part of the indigo has separated out, is cooled until the glacial acetic acid freezes and is then slowly liquefied again. The indigo is now collected on a weighed filter, washed successively with a little glacial acetic acid, hot water, hot dilute hydrochloric acid, and again with hot water until it no longer shows an acid reaction. It is then dried at 100° C. (212° F.) and weighed.

The process is more difficult when vegetable fibres have to be dealt with, as they are more or less soluble in glacial acetic acid, less being dissolved from bleached than from unbleached material, though enough dissolves in all cases to render close attention to this point necessary or the results obtained will be too high.

The solution resulting when undyed bleached material is extracted with glacial acetic acid, gives a flocculent precipitate on dilution (probably cellulose acetate), which is almost invariably soluble in ether, sometimes however only in hot dilute hydrochloric acid, and in order to ensure its removal the indigo filtered off must be washed in turn with both the above solvents.

---

* *Binz* and *Rung*, Zeitschrift für angewandte Chemie, 1902, No. 23.

A good method is as follows: Extract about 10 gr. of dyed cotton with about 150 ccm. glacial acetic acid in a Soxhlet apparatus until all the colour is removed. Then pour the extract into 300 ccm. water, add 150—200 ccm. of ether and shake the mixture thoroughly in a separating funnel. The indigo is suspended in the ethereal layer and the dilute acetic acid is clear so that it can generally be run off at once. Now transfer the indigo to a weighed filter, wash first with alcohol and ether, (only a little alcohol, otherwise the indigo might be partially dissolved), then successively with hot dilute hydrochloric acid and water, and finally dry and weigh.

If analyses are to be made with dyed unbleached goods, it is necessary to make a trial with the undyed material first. The glacial acetic acid dissolves more or less of the impurities attached to the fibre according to their nature, and these are thrown down as a floculent precipitate and may react in a varying manner with respect to the different solvents. It must also be taken into account that the unbleached material loses some of its impurities in the dyeing process, owing to the action of alkalies and acids, so that in order to determine accurately the amount of the impurities extracted by the glacial acetic acid the undyed fibre must be first passed through a vat similar to that used for dyeing, but containing no colouring matter. The extraction with glacial acetic acid is then carried out, and the amount of impurity extracted from the undyed material is directly estimated by weighing.

The difference is often considerable:

Unbleached, undyed yarn lost by direct treatment with glacial acetic acid	1·2 %,
after treatment in a copperas vat containing no indigo and subsequently souring it lost only	0·3 %.

When determining indigo on cotton fibre, 0·3 % was taken as proceeding from the latter and accordingly subtracted.

If the quantity of indigo dissolved is sufficiently large (at least 0·1 gr.), it is always advisable to determine the indigo content by titration according to the hydrosulphite method, (page 14), thus avoiding any error which might be caused by the impurities on the fibre.

IV.

The Indigo Vat.

Indigo Vat.

Indigo itself is insoluble in all solvents which could be made use of in dyeing. Indigo white, on the contrary, which is produced from indigo blue by reduction and contains two atoms of hydrogen more, behaves like a weak acid, and when treated with alkalies forms salts easily soluble in water which behave towards textile fibres like dyestuffs. From these salts the indigo white is re-converted into insoluble indigo blue by oxidation, *e. g.,* by the absorption of oxygen from the air. These remarkable properties of indigo have been turned to account from the earliest times in dyeing and printing and to them indigo largely owes much of its excellent fast character.

By the "reduction" of indigo is to be understood its conversion into indigo white* by means of reducing agents, and this takes place in practice as a rule in the presence of an alkali. This process has always been carried out in vats or tubs, and the dyer has used the solution of indigo white in alkali also in such vessels. In course of time the term "vat" has been transferred from the dyeing vessels themselves to their contents, *i. e.,* to the indigo dye-liquor. By "vat," therefore, is to be understood not only the vessel used for dyeing with indigo, but also the solution of the alkali salts of indigo white in water.

Indigo white possesses an affinity for vegetable and animal fibres, that is, these fibres take it up from its solution and retain it when removed from the vat liquor. The oxygen of the air then oxidises the indigo white on the fibre to indigo, the yellow colour of the dyed material changing first to green and then to blue. This process is known as "oxidising." Vat dyeing proceeds, therefore, in two stages: saturating the fibre with the solution of indigo white, and then precipitating the indigo blue in an extremely finely divided form in and upon the fibre. These two processes together are known collectively as a "dip" in the vat, and such "dips" may be repeated several times as required, the indigo white dyeing the blued fibre afresh without attacking the colour already on it. The indigo blue regenerated from the indigo white by oxidation is deposited on the top of that already present and causes a deepening of the shade. The dyeing operation may therefore be regarded as a purely mechanical deposition of the dyestuff on the fibre, so that indigo may also be considered a "pigment dyestuff."

---

* *Binz* (Zeitschrift für Elektro-Chemie, 1898, No. 9; 1903, 599; Zeitschrift für angewandte Chemie XIX, No. 33) views the reduction as a removal of oxygen from alkali salts of indigo, the reaction leading finally to the production of the same substance, *viz.,* indigo white.

As in the case of most reactions in organic chemistry, the conversion of indigo blue into indigo white is not so uniform and direct that exactly the calculated quantity of the one substance is obtained from the other. When reducing, the treatment with the reducing agents brings about secondary reactions resulting in the formation of products other than indigo white. Unlike the latter these bye-products cannot be re-converted into indigo, and are, therefore, useless for dyeing and represent a loss of dyestuff.

The nature and quantity of these products of decomposition vary according to the reducing agents used and the conditions under which the reduction is carried out. The dyer cannot afford to neglect such losses and must minimise them as far as possible by selecting suitable methods of reduction and working under the most advantageous conditions; he must also bear this loss of dyestuff in mind when calculating the cost of dyeing.

We come now to a closer consideration of the reducing agents which the dyer employs for the preparation of the vat, *i. e.,* for the conversion of the insoluble indigo into its soluble derivative, indigo white, in which form the indigo is primarily deposited on the fibre.

Reducing Agents.

Reducing agents are of various kinds and may be grouped in two classes:

1. Those that reduce by direct chemical reaction.

   There are a great many of these products, so that we consider it sufficient to mention only those which are actually used in practice. Sulphide of arsenic (orpiment, realgar), one of the oldest chemical reducing agents, is met with nowadays only occasionally (for instance among the natives of India), and tin, or stannous oxide, is hardly used at all. Grape sugar (glucose) is still used to a certain extent. The commonest reducing agents at the present day are for dyeing: ferrous sulphate (copperas), zinc dust, and hydrosulphite; for printing: the formaldehyde derivatives of hydrosulphite, and glucose.

2. Those substances causing a specific fermentation process (called the "vat fermentation").

   To this group belong sugars and carbohydrates and nitrogenous substances, *e. g.*, bran, woad, madder, fruits containing sugar, suint, flour, bread, the kind of product used varying considerably according to the practice of the dyer and the readiness with which the substances can be obtained in the various countries.

The kinds of vat are named according to the reducing agents employed, thus corresponding to the first group we have

the copperas vat,
» zinc (zinc-lime) vat, and
» hydrosulphite vat;

and corresponding to the second group:

the various forms of the fermentation vat.

To bring indigo white, which is of an acid nature and insoluble in water, into solution

Alkalies

Alkalies.

are employed and of these the most important are caustic soda and lime.* Ammonia dissolves indigo white only to a small extent, potassium carbonate (potash) has sufficient solvent power for practical use, whilst soda dissolves only traces of indigo. The vats are made up with a greater or less excess of alkali according to their nature and whether they are to be used for animal or vegetable fibre. For if the alkali is removed from the vat liquor by the dyed material or neutralised by the acids which are formed in certain kinds of vat (fermentation vat, or hydrosulphite vat), or which are introduced for example by carbonised wool, the indigo white separates out in the form of white flakes or fine crystals with a pearly shimmer. Since, however, precipitated indigo white is useless in the dyeing process, it is important that the dyer should direct his attention to always having the correct quantity of alkali in the vat.

---

* In the description of wool dyeing it will be seen that animal glue can also under certain conditions to some extent take the place of alkali in retaining the indigo white in solution.

Influence of the physical Condition of the Indigo on the Reduction.

An important point which must not be overlooked is the physical condition of the indigo to be reduced, for since it is a matter of causing an insoluble body to react, it is evident that reduction will be the more assisted the finer the state of division of the particles of dyestuff and the greater the surface exposed to the action of the reducing agent.

If the indigo is too coarse, it resists the reducing process and thus either does not go into solution at all or only dissolves slowly. The result is either a loss of dyestuff or a waste of reducing agent and the vat obtained has less dyeing power. The form and general hardness of natural indigo as brought on the market, necessitates a preliminary grinding involving expense and loss of time, and if this grinding is not very carefully carried out or if the indigo is very hard a portion of the dyestuff may remain undissolved in the vat, so that the result of the dyeing does not correspond to the indigotine content of the indigo. The various brands of Indigo pure, on the contrary, are delivered in such a finely divided state that they dissolve in the vat easily and completely, without previous preparation and with a minimum quantity of reducing agent. The "S" brands are specially remarkable for their extremely fine division and are thus particularly suitable for use in the fermentation vats, for which in this respect the requirements are most exacting.

In order to make the dyer quite independent of the state of division of the indigo, products are now being manufactured which contain the indigo in a reduced form as soluble indigo white or a salt of indigo white.

For instance the various Indigo B.A.S.F. solutions and Indigo vats B.A.S.F. are preparations of this character.

Both of these contain the alkali salt of indigo white in a form which is easily soluble and which keeps for a long time, thereby ensuring a complete utilisation of the dyestuff and an extraordinary ease and accuracy in its use.

Dyeing in the Vat.*

(Indigo Dyeings and their properties.)

Dyeing in the Vat.

The indigo vat may be employed for dyeing all kinds of vegetable, animal, and artificial fibres, the nature of the vat and the method of working being dependent upon the quality or form of the material to be dyed. As a general rule it may be said that vegetable fibres (cotton, linen, jute) are dyed cold, and animal fibres (wool, silk) are dyed warm. In both cases, of course, variations occur, for instance, cotton, wool and silk are dyed in the same cold fermentation vat in Asia, whilst cotton and linen are occasionally dyed in the warm vat (in the Balkan states and Russia). A fundamental difference between the vats used for vegetable and animal fibre is to be found in their alkalinity. Wool and silk, being readily attacked by alkali, must be dyed in weakly alkaline vats; for cotton, etc., similar vats can also be made use of (for instance the fermentation vat in which the sensitiveness of the fermentation process to alkalies limits the alkalinity), but in general more strongly alkaline vats are employed in order to produce the finest shades and ensure good penetration.

An indigo dyeing is produced, as has been explained above, by the oxidation of the indigo white deposited on the fibre. The dyer terms one such treatment, *i. e.,* the impregnation of the fibre with the vat liquor, the removal of superfluous liquor, and the oxidation, a "dip." By repeating such dips a certain amount of dyestuff is deposited each time over the dye already on the fibre and the shade consequently becomes darker; thus dark blues can be dyed either in strong vats with one or two dips, or in weak vats with a good many dips. If we bear in mind that the dyeing is really a mechanical deposition of the indigo blue in the fibre, it will be seen that a dyeing must be better and faster the more internally this deposition in the fibre takes place. To ensure fastness to rubbing, that is resistance of the dyestuff to mechanical friction, it is of the highest importance to the dyer to prevent the dyestuff from being precipitated too quickly or in too great amount at one time upon the fibre. That is to say, dyeing should not be carried out in too strong a vat or with too few dips. Absolute fastness to rubbing cannot be attained, as indigo has really no chemical affinity for the fibre and merely adheres to it as a pigment dyestuff. A certain amount of the dye can always be rubbed off, but the greater part remains firmly attached and resists the severest washing and rubbing. Indigo is naturally deposited on the fibre more slowly and in a finer state from a weak than from a concentrated vat, so that for the same shade a dyeing would be faster when produced in several dips from a weak vat than with fewer dips from a strong vat. When working correctly, therefore, each shade should be obtained by a proportionate number of dips and in vats of corresponding strength.

---

* See *Binz* and *Rung*: "Zur Theorie des Färbeprozesses in der Indigoküpe," Zeitschrift für angewandte Chemie, 1902, No. 25.

Influence of the Reducing Agent on the Dyeing.

The importance of the condition of the vat will readily be perceived when it is considered that only the dissolved indigo white is capable of dyeing. Only the completely dissolved indigo white can penetrate the fibre and afterwards, on oxidation, cause the indigo to separate in the requisite state of fine division. Indigo which has not been reduced is deposited on the surface of the material to be dyed in the form of coarse particles: such a dyeing cannot, of course, be fast. The maintenance of the normal condition of the vat depends above all things on the correct proportion of the reducing agent. We have already seen that the reducing agent is used to convert the indigo blue into indigo white, but besides this, each vat must have a certain surplus of reducing agent, which, however, must not exceed a definite amount. Dyeings could of course be obtained from an indigo white solution by itself, but after a short time such a vat could not be used further, as the least quantity of oxygen coming into the vat either with the goods or through contact with the air would cause a separation of indigo blue which in itself is incapable of dyeing. A portion, therefore, of the extra reducing agent serves to keep the indigo during the whole period of dyeing in the form of indigo white, in which state alone it is of use for dyeing.

During oxidation also, the excess of reducing agent plays a part, as it prevents a too rapid and premature separation of the indigo. When the goods leave the vat they are permeated with mechanically attached indigo white solution in addition to the quantity which is organically incorporated. If no reducing agent were present, the oxygen of the air would at once act on the indigo white and immediately precipitate the whole of the indigo, so that the fibre would be loaded with unfixed, coarsely separated indigo, *i. e.*, the dyeing would not be fast but would rub badly and wash off considerably. An excess of reducing agent, on the contrary, prevents this immediate action of the oxygen of the air and so retards the oxidation of the indigo white that the excess of dye liquor can be removed and returned to the vat before the precipitation of the indigo blue begins, and the dyestuff is thus deposited in the fibre gradually and in a fine state of division.

A striking proof of these principles is afforded by the behaviour of wool in the hydrosulphite vat. If wool is dyed in a vat possessing a strong reducing action, it will be seen that after prolonged oxidation hardly any colour is removed by washing with water even in the case of dark shades, but if, under otherwise similar conditions, the vat contains too little hydrosulphite and the oxidation to blue has proceeded quickly, a large part of the colour, often as much as half, will be lost on washing.

It must also be noted that the quality and previous treatment of the goods to be dyed have a decided influence on the result. It will readily be understood for example that wool which has not been scoured sufficiently, cannot absorb indigo white in the way necessary to render an intimate combination with the fibre possible, and again open, loose material, for instance, takes up the dyestuff better than closely woven cloth or tightly twisted yarn. This difference is very noticeable in the case of cotton yarn and cotton piece-goods. The former is much more easily and completely dyed through and loses much less indigo when rinsed than piece-goods which are naturally composed of firmer threads. In the case of very heavy and thick goods, satisfactory penetration can only be obtained by means of special operations, *e. g.*, by giving much longer dips and using squeezing rollers.

The foregoing observations lead to the conclusion that fastness is due solely to the method of working and the condition of the vat, and not to the kind of indigo used or its composition. The idea, for instance, that certain constituents of natural indigo, such as indigo gluten or indigo red, tend to produce faster dyeings, had never really any foundation, and practical experience has shown in every case that it is incorrect. A comparative test, such as given below, will show very simply that a dyeing with natural indigo is not any faster than one with Indigo pure.

Dye two hanks of cotton yarn of similar quality in an exactly similar manner in two series of 3 or 4 vats set with natural indigo and Indigo pure respectively to the same shade of dark blue. Commence dyeing in the weakest vat and proceed to the strongest, the corresponding vats of the two series containing similar amounts of colouring matter. If the dyeings obtained in this way are tested in pairs by rubbing and soaping in the same bath, both cold and at the boil, and with the addition of soda and caustic soda, it can be proved with absolute certainty that the hanks dyed with natural indigo and those dyed with Indigo pure, behave in exactly the same way. When testing the fastness to bleaching weak solutions only of bleaching powder (0·4 ^{0} Tw.) should be used, otherwise a portion of the dyestuff will be rapidly destroyed. Rigorous tests with strong solutions and at an elevated temperature are as useless in the case of natural indigo as of Indigo pure B. A. S. F. and harmonise neither with the treatment in actual use nor with the character of the dyestuff. Natural indigo and Indigo pure slowly become paler at the same rate in weak solutions of bleaching powder and are speedily destroyed by strong solutions.

Part played by Alkali in the Vat.

With regard to the part played by alkali* in the vat, we have already referred to the difference between the vats for animal and those for vegetable fibres. Alkali is not only to be considered as a solvent for the indigo white, but it also exerts considerable influence on the process in wool dyeing. In order to take up indigo white, the fibre must split up the alkali salt of indigo white and the absorption is naturally more difficult the more alkali present. On the other hand, however, the shade is evidently also influenced by the action of the alkali on the physical state of the dyestuff precipitated on the fibre. As a general rule it can be said that strongly alkaline vats, of course within a certain limit, produce brighter shades than less alkaline ones. The quantity must be regulated with regard to the kind of alkali and the nature of the fibre. For example, a slight excess of strong alkali, such as caustic soda or lime, greatly hinders the deposition of indigo white on wool. In this case bright reddish shades are produced by adding to the vat a weak alkali such as ammonia, which does not affect the wool fibre and at the same time does not delay the deposition to the same extent as the strong alkalies mentioned above. Since cotton, on the contrary, is not affected by alkali, the quantity of the latter should always exceed a certain minimum, otherwise the resulting shades will be dull.

---

* See also *Binz* and *Rung,* Zeitschrift für angewandte Chemie, 1900, No. 17, and 1902, No. 25.

Incorrect views as to the influence on the shade of the condition of the vat and the method of working are still very common, so that it is necessary to consider these factors somewhat more fully.

Indigo Red. Behaviour in the Vat.

The idea is occasionally met with that the indigo red contained in vegetable indigo has a favourable influence upon the shade. With regard to this point, *Schwartzenberg* and *Schwartz* (Bulletin de la Société ind. de Mulhouse X, 413, 425), of whom we have already spoken, as a result of exhaustive researches on the bodies accompanying indigotine in vegetable indigo have thoroughly examined the question as to the part played by indigo red in dyeing and have come to the following conclusion:

In dyeing indigo red is partially precipitated on the fibre along with the blue, but it improves neither the beauty nor the fastness of the shade and is not necessary for the production of a fast, bright blue colour. As a matter of fact, when present in larger quantities it may even make the shade dull and unsightly.

More recently *Tulleken* (Bulletin van het Koloniaal-Museum te Haarlem, No. 20, 1899) carried out a series of comparative dyeings with and without the addition of the various bodies that accompany natural indigo, especially indigo red, and obtained the opinion of a number of competent judges upon them. In this way he arrived at a similar conclusion which he expressed as follows:

Conflicting opinions are often expressed when judging dyeings produced in the indigo vat, and it may therefore be said that the secondary substances found in natural indigo but very slightly influence the shade, so slightly in fact that the occurence of these bodies in Java indigos whether containing much or little indigo red is of little or no importance from a practical point of view. *Merrit Mathews* also in a recent paper (Society of chem. Industry, Sect. New York, Chemiker-Zeitung 1902, page 151) came to the conclusion that indigo red can have no favourable influence whatever upon the shade.

Indigo red of exactly the same composition as in natural indigo can also be prepared artificially.* It is to a certain extent analogous to indigo blue in that it is transformed into an indigo white in the vat, which is also deposited on the fibre and is oxidised to a dyestuff on exposure to the air. If the various processes are examined which take place when indigo red is reduced, it will first of all be noticed that in the **warm vat** (for wool) the greater part of the red is destroyed and takes no further part in the dyeing, and in addition that the smaller portion which has not been destroyed is changed into blue after being a short time in the vat. This observation has also been recorded by *V. Fasal* (Deutsche Färberzeitung, 1896, page 196) and *J. Dépierre* (Teinture et Impression III, 232). The result, however, when dyeing, for example in a hydrosulphite vat set with indigo red is not a pure blue, but a dull dingy blue colour is obtained even on the second day. In the **cold vat** (for cotton) that part of the red which is not destroyed remains chiefly as such but does not produce, as is sometimes wrongly stated, a pure red colour giving a reddish blue in combination with indigo blue, but dull, reddish grey shades which make the blue of the pure indigo dyeing considerably duller. Further, shades obtained from indigo red are not very fast to washing.

Only when dyed as a sulphonic acid on wool in an acid bath, does indigo red really yield red-violet shades. This property, however, is anything but desirable in the case of indigo extracts and carmines so that, as every manufacturer of indigo preparations knows, the Java brands, which contain a large proportion of indigo red, are useless for this purpose.

It follows, therefore, from our remarks on indigo red that it is most advantageous for the dyer to have a brand of indigo which is entirely free from red colouring matter. Indigo pure B.A.S.F. is an indigo of this kind.

---

* *Schunck* and *Marschlewsky*, Berl. Ber. 1895, 28, I, 539.

It must be expressly mentioned that the shade of an indigo dyeing is dependent only on the form in which the indigo is deposited on the fibre, and the red tone, so far as at present known, is the result of a crystalline deposition. Now this form of deposition can easily be brought about by selection of the right kind of vat and by the method of working during dyeing and afterwards, *e. g.,* in souring, regulating the temperature when drying, and steaming. Indigo pure dyes redder than a natural indigo containing indigo red, because it can be separated in a suitable form as a pure dyestuff without admixture of substances which would dull the shade. A detailed description of the methods of working will be found in the special chapters, but it may be mentioned here as an example that the "glue preparation" of the fibre (described later on under cotton dyeing) also increases the red tone, thus directly proving that the cause of this appearance is purely physical.

Having now explained the fundamental principles upon which correct indigo dyeing depends, we may now consider in general the

Properties of an Indigo Dyeing in respect of Fastness.

Properties of Indigo Dyeing in respect of Fastness.

Indigo, whether artificial or natural, ranks among the fast colours, and it is owing to its permanence that it has always been one of the most widely used dyestuffs. Its resistance to the effects of water, soap, alkalies, acids and atmospheric influences, gives it the advantage over almost all its blue competitors that it preserves its pure blue tone unchanged in spite of the continued action of the various influences, such as washing, light, etc. to which it is exposed in wear, although the shade may become somewhat paler owing to a partial destruction of the colouring matter. Only in the case of very pale delicate blues does the colouring matter, otherwise so permanent, exhibit a certain sensitiveness which cannot be overlooked. For instance, very pale dyeings on wool change in shade somewhat when steamed and exposed to heat (in decatising). Since the dyestuff, as described above, is mechanically attached to the fibre, indigo dyeings are naturally not of the greatest fastness to rubbing and milling.

The rubbing off is of course less marked in the case of wool, owing to its scaly structure, than in the case of the smooth cotton fibre. This insufficient fastness to rubbing should be ascribed, strictly speaking, only to that portion of the dyestuff which in dark shades is attached to the outside of the fibre, when this is once removed that portion inside the fibre withstands a mechanical removal all the better. The fastness to light is as a rule sufficient for all practical purposes; medium and dark shades are not noticeably affected, pale shades fade to some extent in the course of time.

Indigo withstands the action of chlorine to a certain degree only and a considerable amount of care must therefore be taken in bleaching woven goods containing indigo dyed yarns. In the chapter dealing with the after-treatment of dyeings on cotton yarn will be found a process for increasing the fastness of such yarns to bleaching with chlorine (page 59).

A fact which is theoretically interesting and at the same time practically important, is that certain derivatives of indigo are much faster to chlorine than indigo itself. Thus the reddish toned Indigo pure B. A. S. F./*R* is rather better in this respect than indigo, and the greenish-toned Indigo pure B. A. S. F./*G* is almost perfectly fast.

In the foregoing section the conditions that are of importance in indigo dyeing have been fully discussed, and it has been indicated upon what factors a good result depends. The production of fast and beautiful shades does not depend on the action of the impurities contained in vegetable indigo, nor on the employment of one or other of the commercial brands, Bengal, Oudh, Java, or whatever it may be. Indigo is always indigo with all its inherent properties and the absence of substances that are not indigo can only be of advantage in the dyeing process. The secret of certain success can be expressed in a few words:

Proper treatment of the indigo in setting the vat,
keeping the vat in good condition and working it correctly.

1st part.

Indigo pure B. A. S. F.

and its

Employment

in the

Dyeing of Cotton.

The Dyeing of Cotton and other Vegetable Fibres.

1. General Remarks.

Dyeing of Vegetable Fibres.
General Remarks.

By far the greater quantity of indigo consumed is used for dyeing vegetable fibres. As is well known, cotton, linen or half-linen clothing materials dyed with indigo are produced on a large scale in all countries. Cotton is dyed in all imaginable shades with indigo, from pale blue for blouses and medium blue for Chinese and oriental clothing to the dark blue-black of Saxon and Silesian aprons or Japanese kimonos.

Cotton is dyed in various forms in the vat, usually, however, either as yarn or as piece-goods, less frequently as loose cotton, sliver, slubbing, or roving. Yarn is dyed either in the hank by hand, sometimes with the aid of mechanical wringing apparatus,* or as warp, cops, or cheeses, by mechanical means. In many Eastern countries (China, Japan, etc.) piece-goods are dyed in large quantities by hand, in other countries, however, mechanical appliances such as the dipping frame and the continuous vat are in general use. In some cases roving and sliver are also dyed in machines, the former in the continous vat, like piece-goods or warps, the latter on bobbins. Loose cotton can be dyed in a basket by dipping, or in a machine provided with an arrangement for circulating the liquor.

---

* The firms *Juan Regordosa & Luis Regordosa,* Barcelona (Spain), and *Planella & Cie.,* Barcelona, have quite recently patented machines for dyeing hanks.

Of the various forms of vat, the following may be employed for the dyeing of cotton, linen, etc.: the copperas vat, the zinc-lime vat, the different kinds of hydrosulphite vat, and the cold or warm fermentation vats. The kind of vat to be employed depends upon the nature of the material to be dyed and whether it is to be dyed by hand or in machines.

Dyeing is generally carried out cold, only the fermentation vat being occasionally used warm in certain countries by the small dyers and as a home industry. Occasionally the hydrosulphite vat is slightly warmed in order to ensure better penetration.

Test whether a Fibre has been dyed with Indigo.

To test whether a dyeing has been made with indigo, burn a small piece of the pattern to be examined to ashes on a white glazed plate. If a light blue stain is formed which turns yellow on treatment with concentrated nitric acid, indigo is present.

2. The Dyeing of Yarn.

Dyeing of Yarn.

Before dyeing, the yarn must be thoroughly boiled out, either with or without pressure, preferably with the addition of a little soda or caustic soda. The impurities added during spinning must be removed, otherwise uneven shades are produced which rub off badly. After boiling out, hydro-extract or wring out, and without drying enter in to the vat. Care must be taken that the yarn is not exposed too long to the air after boiling out, or otherwise it may dry in places and show up striped and spotted when dyed. More yarn should not be entered into the vat than the workman can conveniently turn and wring out, or the dye liquor does not penetrate the fibre evenly and the liquor removed with the goods cannot be completely and evenly wrung out.

Narrow, deep, rectangular vessels are used as dye-vats, either made of iron or built of cement. Wooden tubs lined with cement can also be used or even, on a small scale, simply narrow wooden barrels from 4—6 feet in height.

The following dimensions are suitable for a rectangular cement vat: 26 inches broad, 32 inches long, and 5—7 feet deep.

The yarn is dyed on sticks. The hanks are moved slowly about keeping them as far as possible under the liquor, and turned from time to time, without drawing them taut, till the fibre is completely saturated. Directly on leaving the vat, the hanks are wrung out on the wringer fixed over the vat then once more on the peg and laid out to oxidise. Here also care must be taken that the yarn does not become dry in patches between the dips, otherwise uneven dyeings result. The oxidation must be complete before another dip is given.

A vat generally takes three sticks with 2 lbs. yarn each which are turned alternately. As soon as one stick is wrung out, another is entered into the vat, so that three sticks are always being treated at the same time.

One man attends to the turning in the vat and the first wringing, and another to the second wringing out on the peg and the laying out to oxidise.

Dyeing is always begun in a weak vat and continued in stronger vats until the desired shade has been obtained. A row or set of vats of increasing strength is thus necessary,* the strongest containing about 0·3 % of indigotine. A series of 6 vats for dyeing dark blue in as many dips may for instance be set as follows: The first vat for blueing the white yarn is set with 1—1½ lbs. Indigo pure 20 % per 100 gallons liquor, the second, third, fourth, and fifth with 3, 5, 8 and 13 lbs. respectively and the sixth or finishing vat with 15 lbs. indigo. When the first vat is exhausted it can either be replenished or, if the full series is in use, it is re-set as the strongest vat and dyeing commenced in the second vat, and so on in turn.

To dye a sky blue shade give two dips in the weak vats, for medium blue about 4, and finish a dark blue in 6—8 dips. The more dips given in the production of a shade the faster it is to washing and rubbing. Dyeing too quickly always reduces the fastness to rubbing. If a dyeing is to meet the ordinary demands as regards beauty and fastness, it must be produced only from completely reduced, clear vats. If a vat has lost its good condition, dyeing must be stopped until it has been once more made fit for use by suitably "springing."

---

* The fermentation vat is an exception, vats of equal strength being generally employed.

Although cotton is not sensitive to alkalies, still it is well to keep as closely as possible to the quantity of lime or caustic soda given in the recipes, if good dyeings are to be obtained. If the alkali content sinks under a certain limit, dull, uneven shades are produced, whilst too much alkali, particularly caustic soda, retards absorption and also produces uneven shades.

Coppery Shades.

If a shade as reddish and coppery as possible is desired, the drying must take place as hot as possible or the dyed goods must be steamed. The damp heat brings about a physical change in the indigo fixed on the fibre causing the shade to appear redder. The coppery tinge produced in this way disappears, however, on washing. Another method of obtaining a specially reddish tone consists in souring, rinsing, and drying the goods between the last but one and the last dip.

Sometimes a dark shade is required without any coppery tone. This is effected by finishing in a weak vat and not in the strongest, as usual.

It may be mentioned here that the shade is always made duller by the sizing operation unless a dyestuff is added to the size, which will impart a bright tone. We give below (page 56) special methods for producing duller shades should these be desired.

In the case of vats containing lime, the goods should be soured before being rinsed (about 2 pints sulphuric acid or hydrochloric acid per 100 gallons water); but if the vats contain caustic soda, it is sufficient simply to rinse with water. After rinsing, the yarn is dried. Dyeings which have been dried before being soured or rinsed have a rather deeper shade.

Vats employed for the Dyeing of Yarn.

For dyeing yarn the following vats are employed and recipes for them will be given separately further on:

the zinc-lime vat,
» copperas vat,
» hydrosulphite-soda vat,
» bisulphite-zinc-soda vat,
» fermentation vats.

The zinc-lime vat is best suited for this purpose and the one most generally used. The copperas vat is being less and less used, as it does not work rationally owing to the great loss of indigo in the vat and the large amount of sediment which renders it necessary frequently to exhaust the vat and set it afresh. The hydrosulphite vat is not much used for dyeing yarn in the hank, because the caustic alkali renders the working by hand difficult, but when working in machines its great advantage of giving a clear vat free from sediment is apparent. The hydrosulphite vat is thus to be recommended in all cases where the yarn, whether as hank or as warp, is mechanically drawn through the dye-liquor.

For continuous working, which aims at as large an output as possible, the hydrosulphite vat also takes precedence of the others inasmuch as it can be preserved in the normal state of reduction without ceasing work by simply adding hydrosulphite. It has thus the greatest working capacity. The bisulphite-zinc-soda vat comes chiefly into consideration for the same purposes as the hydrosulphite-soda vat, but it has the disadvantage in comparison with the latter of not being quite free from sediment; there is also a certain loss of indigo through reduction.

The fermentation vats are used warm and cold for cotton yarn. The warm vats, such as the potash vat, the bread vat, the bran vat, are used more or less in almost all European countries, principally in Russia, Italy and the Balkan states, and chiefly in the country districts and for dyeing on the small scale. The cold or merely slightly warm fermentation vats have a very wide application in countries other than European. The enormous quantity of indigo consumed in Asia, Africa and Central America is almost entirely used in one or other of the various forms of the cold fermentation vat. With regard to the cost of reducing agents, the fermentation vat is the cheapest, as waste products of various kinds, which are otherwise worthless, can be used as ferments. It has, however, only a small working capacity, as the fermentation process necessary for the reduction of the indigo, proceeds very slowly. Goods dyed in it acquire a peculiar odour owing to the fermentation process, and in many districts this is demanded by the customers. Further, in comparison with the other forms of vat, it produces (especially when worked warm) a shade which is less bright and coppery. This difference is due to the slow absorption of the dyestuff which makes the dyeings very fast to washing. If an indigo dyeing has to be rapidly prepared and must at the same time have the characteristic odour of the slow fermentation vat, the goods should be dyed in the copperas or zinc-lime vat to about the shade required and then finished in one or two dips in the fermentation vat. The vat odour can also be artificially prepared (see page 57).

Appliances for the Dyeing of Yarn.

Of the appliances for dyeing yarn in the hank we may mention here the dyeing machine on Spencer's system, which is intended to save the labour of wringing out the yarn by hand. A workman lifts out the yarn and lays it on two hooks placed over the vat facing one another. One of them is then twisted round and the other which is capable of a sliding motion is loaded down by a weight and thus keeps the hank taut.

For the continuous dyeing of yarn in the hank special machines have been constructed by Mess^rs. *Juan Regordosa & Luis Regordosa* and Mess^rs. *Planella & Co.*, both of Barcelona, in which the hanks in a continuous chain are passed through the vat and after leaving the liquor are immediately squeezed out between rollers. The working of the machines is quite simple and enables a considerable saving to be effected in general working expenses.

This method does away with all hand work in dyeing and wringing, and has a very good working capacity. If the necessary precautions are taken the fastness is as good as when the yarn is dyed by hand.

3. Dyeing of Warps.

Dyeing of Warps.

Cotton is often dyed in the form of **warps.** The advantage consists in the greater output by reason of the continuous working, and in the saving of labour, due to the necessity for winding off the hanks again being obviated. Dyeings on warps are remarkable for their evenness, since the squeezing through rollers removes the liquor more evenly than the wringing out of hanks by hand. On the other hand, however, the penetration of the yarn is not so complete as when dyed in the hank owing to the rapid passage through the vat.

Warps are passed through the vat in the same way as piece-goods in the continuous vat over a set of guide rollers, either backwards and forwards horizontally or up and down, and after

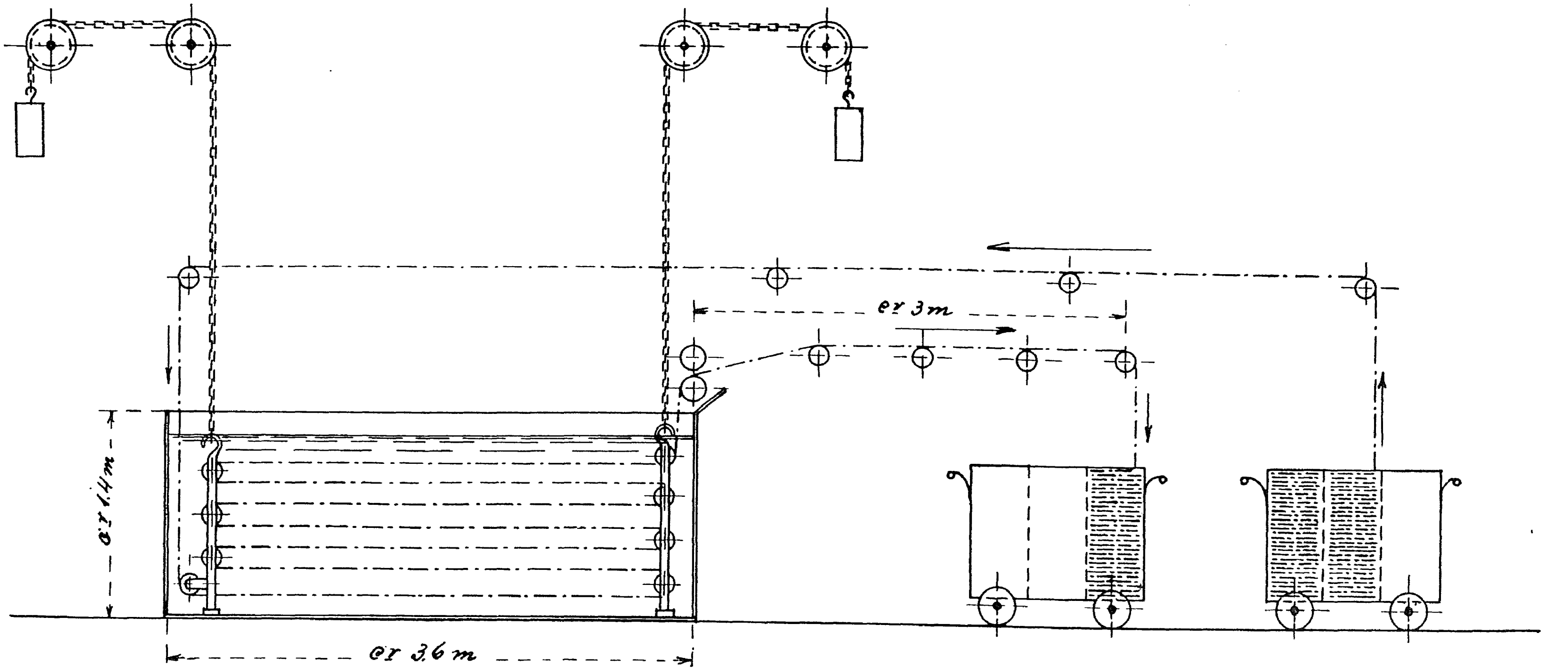


Fig. 2. Continuous Vat.

each dip they are squeezed out between rollers and oxidised by a short air passage over or behind the vat. About eight or ten warps of the thickness of a finger are run side by side through the vat, each dip representing about thirty seconds in the vat. Figure 2 shows such a warp-dyeing vat, the warp runs in the direction shown by the arrow. In order to keep the warps running smoothly and avoid entanglement with those adjoining, they are kept apart while running by means of pegs. Several vats may either be arranged one behind another, so that the warp each time after being squeezed and oxidised passes directly into the vat immediately following, or the warp is led into travelling boxes and carried to the next vat. In the former case the air passage must, of course, be long enough for complete oxidation before the warps enter the next vat, in the latter case the hanks do not need to be completely oxidised when they come into the boxes, since oxidation will be completed in the boxes themselves. It is advisable to mount the guide rollers on a common frame which can be moved from one vat to another. If the rollers are arranged horizontally the duration of the dips can be regulated by immersing the frame more or less in the vat. The warp is dried on cylinder drying machines.

To dye warps as described above the zinc-lime and the various hydrosulphite vats are employed. If a zinc-lime vat is used, the dye-vessel must be deep enough to prevent the warp coming into contact with the sediment at the bottom. The oxidation passage must be rather longer with the hydrosulphite vat (or bisulphite-zinc vat) than with the zinc-lime vat, because the oxidation in the air takes place more slowly owing to the hydrosulphite adhering to the yarn.

4. The Employment of Indigo pure B. A. S. F./*R* and Indigo pure B. A. S. F./*G* in dyeing Cotton Yarn.

Indigo R and G in the Dyeing of Cotton Yarn.

The *R* brand is suitable for producing a specially bright, reddish toned blue, and the red tint can be varied as desired by using it either alone or in combination with the ordinary brand. Indigo R can be dyed with indigo from a mixed vat, or indigo dyeings can be topped in a vat set with Indigo R alone.

A vat is set and yarn is dyed with Indigo R in the same way as with ordinary indigo. The purest shades are produced in the hydrosulphite vat, but the zinc and copperas vats may also be employed.

Indigo pure B. A. S. F. / *G* produces a full, pure, greenish blue the chief merit of which is its excellent fastness to chlorine (bleaching). On this account it deserves special attention for coloured woven goods. Indigo G can also be dyed from a mixed vat with ordinary indigo or with the *R* brand. The method of working and the kinds of vat are the same as those for ordinary indigo.

5. Special Methods of Preparation and After-treatment in dyeing Yarn.

Special Methods of Preparation and After-treatment in dyeing Yarn.

Finishing, as has been stated already, affects the shade of indigo dyeings. As it is often desired to give a shade a blackish tone we give below the various means for producing this effect.

a) By sizing.

Darkening of the Shade by Sizing.

Indigo dyeings are made much deeper and duller by a finishing paste consisting of starch paste and fat.

Apart from the method of working, the extent of this effect depends firstly on the nature of the finishing paste, and secondly on the depth of the shade of indigo.

All the thickening agents (dextrine, British gum, ordinary starch) commonly used have a dulling effect. Ordinary starch has by far the most powerful action.

The nature of the fat is less important, but solid fats are to be preferred to oils. It is practically a matter of indifference whether tallow or lard is taken.

The depth of the shade of indigo has also an important influence on the extent of the dulling, for while blue shades are only slightly darkened, the dark, reddish shades are at once blackened.

If the yarn is to retain its soft handle, the starch and the fat should be used in equal proportions, but if the yarn is at the same time to be sized, *i. e.,* stiffened, the quantity of fat must be diminished or omitted altogether.

The proportion by weight of the finishing mass to the goods and its concentration can be varied within wide limits. 1 lb. of starch and an equal quantity of fat per 100 gallons of size are sufficient to blacken in one passage yarn dyed in a dark shade.

It is scarcely necessary to mention that the nature of the finishing does not diminish in any way the typical reactions of an indigo dyeing.

Addition of ferrous sulphate (copperas) to the size:

Sizing with addition of Copperas.

To obtain specially dark, blackish shades, add about 3—5 lbs. of copperas dissolved in a little water to 100 gallons of sizing paste. The quantity of ferrous sulphate taken depends on the degree of blackening desired.

b) By means of an iron bottom.

Iron Bottom.

The goods are passed, before dyeing, through a solution of 5—10 lbs. copperas per 100 gallons water at a temperature of about 100° F., wrung out (or, if warp, squeezed out), and dyed without rinsing.

The quantity of copperas taken varies here also according to the extent of blackening desired.

c) By topping with iron.

Iron Topping.

The finished dyeing is rinsed in cold water containing about 5 lbs. copperas per 100 gallons, well wrung out, and dried at once.

When discussing the fermentation vat we mentioned that a peculiarity of this kind of vat consists in its imparting to the goods dyed in it a specific odour. The same smell can be given to dyeings obtained from other kinds of vat by after-treatment with

"Vat-odour,"

Vat-odour on Cotton Yarn.

which we deliver in the form of a white to yellow powder. It is used as follows. About 1 oz. of the vat-odour is well stirred into $^1/_2$ gallon of hot water and the whole, while warm, poured into about 25 gallons of cold water. The dyeings are then passed through this water, which serves at the same time for rinsing, and dried at a moderate temperature.

Preparation with animal glue

Glue Preparation.

is chiefly of interest for piece-goods and is described in this connection (page 68). The method of working there given also applies to yarn.

6. Indigo in Combination with other Dyestuffs.

Combination with other Dyestuffs on Cotton Yarn.

When dyeing yarn, indigo is often combined with other dyestuffs, either for shading (brightening) or to save indigo. These dyestuffs are generally used for topping, *e. g.,* in finishing, less commonly for grounding. For topping, the Oxamine Blue and Indoine Blue brands are suitable, also, especially as additions to the finishing paste, the Methyl Violet and Victoria Blue brands, etc.

Grounding with Kryogene Black.

The Oxamine Blues may be used for bottoming, but not Indoine Blue, since the latter is attacked in the vat. In order to effect a saving in indigo, where a pure indigo dyeing is not demanded, the yarn may be first dyed a pale to dark grey with $1^1/_2$—5 $^0/_0$ of one of the Kryogene Black brands by the usual process and then topped in the indigo vat. The ground of Kryogene Black behaves in a remarkable manner like a mordant, accelerating to a considerable degree the rate at which the indigo is taken up; for this reason when dyeing in the vat an extra amount of care is necessary, and in order to avoid streakiness, dyeing must be commenced in a weak vat.

7. Increasing the Fastness of Dyeings on Yarn.

Increasing the Fastness of Dyeings on Yarn.

In the description of the methods generally in use for the dyeing of yarn attention was drawn to all the points which must be observed if dyeings as fast as possible to rubbing and washing are to be obtained. If the demands with regard to fastness are very exacting, a particularly good fastness to washing may be ensured by lightly soaping and rinsing the yarn between every single dip, so that each time all the mechanically adhering dyestuff is washed away.

An improvement in the fastness to chlorine and — although to only a slight degree — in the fastness to washing also, is brought about by a treatment of the dyed yarn after rinsing with Turkey red oil and acetate of alumina. This is carried out as follows:

The indigo dyed yarn is turned in a bath consisting of 10 parts of Turkey red oil F (sulphoricinoleate) and 90 parts of water until it is evenly penetrated, wrung out and thoroughly dried in 12 hours at 120—160° F. The yarn is then impregnated with acetate of alumina 9° Tw., wrung out, and again dried. The improvement in fastness is due to the indigo being covered with a protective layer of the aluminium salt of the fatty acid.

8. The Dyeing of Piece-goods.

(Cotton, Linen, Cotton and Linen Unions.)

General Remarks.

Dyeing in the piece is carried out for the production of plain blue goods and for discharge and resist work. Pieces, like yarn, must be thoroughly cleansed by boiling out before dyeing, since a well washed piece is indispensable for the production of dyeings of the greatest possible fastness. In the successive operations of the dyeing process the same precautions are to be observed as in yarn dyeing, *viz.,* completely reduced, clear vats, which are free from undissolved indigo; not too rapid dyeing and thorough rinsing after dyeing to remove unfixed dyestuff and the salts contained in the vats. Further the remarks made with regard to the influence of drying on the shade in yarn dyeing apply here also, for certain special styles the coppery tone obtained by steaming is increased and lustre added to it by subsequent mangling or hot calandering. Dyeing is always commenced in weaker and continued in stronger vats. In dyeing pieces printed with a resist paste in the dipping vat they are first dipped in a "wetting-out vat," which may be an almost exhausted vat or merely a solution of lime; further details on this point are given in the chapter on resist printing. For special purposes the ordinary rules are set aside, *e. g.,* in the production of the so-called Guinea styles for export goods, distinguished by their dark, coppery shade, which is not only not required to be fast but actually must rub off and show imperfect penetration. In order to achieve this effect when desired, the goods are rapidly dyed in concentrated vats containing 6—7 lbs. indigotine per 100 gallons, acidified, rinsed, dried hot and calandered hot.

Guinea Style.

Vats employed.

The same kinds of vats are employed in piece dyeing as for cotton yarn, and the advantages and disadvantages of the various vats set forth in the description of yarn dyeing are found here also.

The vats most largely employed in Europe are the zinc-lime and hydrosulphite vats; the fermentation vats are not suited for practical working under European conditions but these vats — especially those which are worked cold — find extensive employment in tropical and oriental countries in the dyeing of cotton piece-goods.

Piece-goods may be dyed either in the dipping vat or the continuous vat.

Dipping Vat.

The **dipping vat** is especially suitable for the dyeing of heavier goods (apron materials, heavy drills, linen, cotton and linen unions, pilots) and for resist work on cotton, linen, and unions. It should be used in all cases in which the penetration of thick material has to be brought about by a long immersion in the vat, and serves, therefore, also for bottoming piece-goods which are difficult to penetrate, these being subsequently topped in the continuous vat.

The dipping vats are best constructed of cement or iron, wood is not sufficiently durable. The cement vats are square or round with a diameter of about 4 ft., and 8—10 ft. deep. The

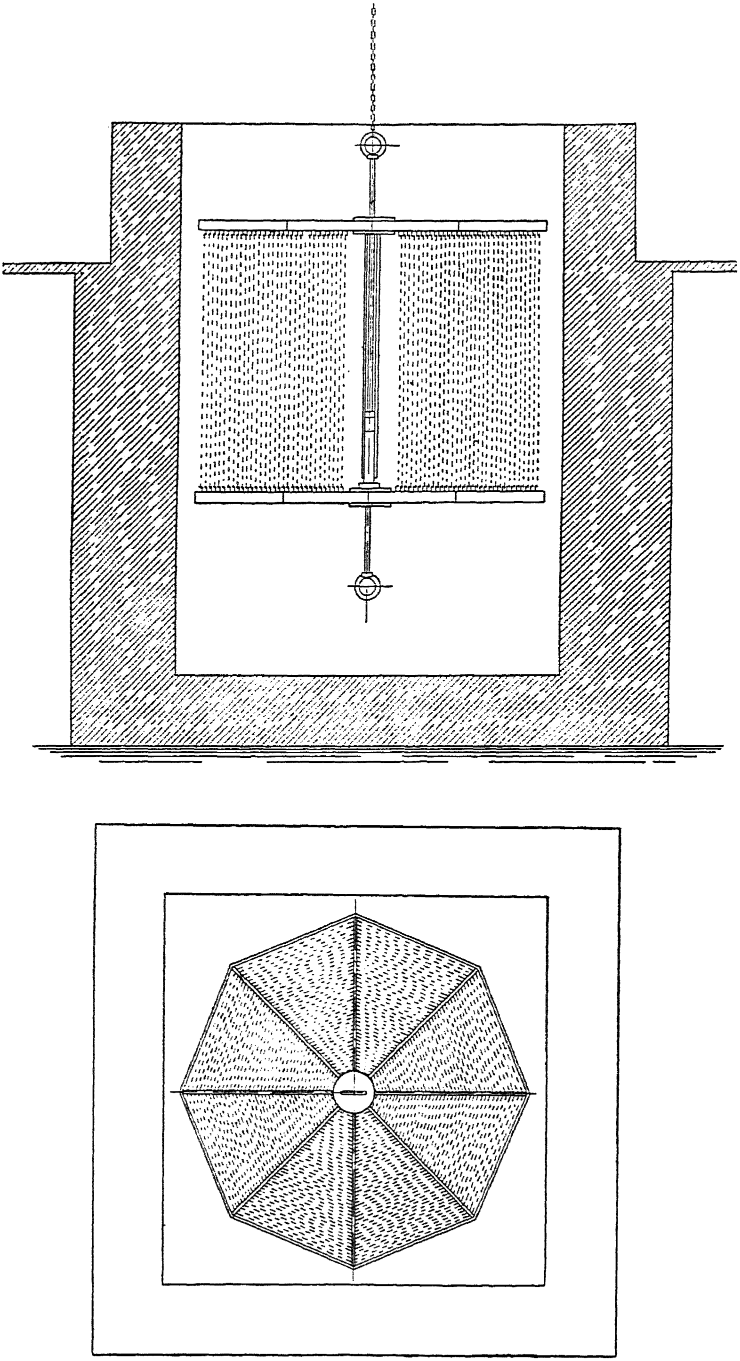


Fig. 3. Dipping Frame and Vat.

edge of the vat should not be too high above the floor (at most 2 ft. 6 inch.) for convenience in entering and taking out the pieces and in stirring the vat. Iron vats are made round and of similar dimensions to the cement vats, and if possible they are not sunk in the floor but rest upon it. This arrangement has the advantages that repairs are easily carried out and that the vat can readily be emptied by an outlet at its lowest part. Above the series of vats, which are arranged as far as possible side by side, is a travelling pulley for lowering the dipping frames into the vats.

The zinc-lime vat is best adapted for dipping vats, for pale shades the hydrosulphite vat may be employed, but in medium and especially in dark shades this vat tends to give uneven dyeings. This is due to the fact that the hydrosulphite is not removed from the goods by squeezing as in the continuous vats and the defect is most noticeable in the case of heavy goods (linen, unions, cotton drills).

Dyeing in the Dipping Vat.

For dyeing in the dipping vat the piece is hooked on to the dipping frame,* or, in the case of heavy materials which hang evenly in the vat by their own weight, it is hung zig-zag on a wooden or iron frame.

Figure 3 shows a dipping frame used in this method of dyeing, consisting of a framework with 6—8 arms on which the piece is stretched in a narrow spiral by means of small hooks. The distance between the arms can be regulated by a screw on the axle, so that the material can be always kept in a stretched condition and the folds do not touch one another. Sometimes it is desired to dye a dark shade on one side of the piece only and to leave the back of the cloth as light as possible, *e. g.,* with pilots for trouserings and for resist styles on dress goods. In this case two pieces are laid together back to back and the frame frequently screwed up, so that the pieces lie closely to one another, and the liquor penetrates as little as possible to the back.

The frame is slowly let down by means of the pulley into the vat, so that the piece is completely immersed, and since any contact with the sediment must be avoided the vats must be sufficiently deep when the zinc-lime or copperas vats, which contain much sediment, are used.

---

* Made by *C. H. Weisbach,* Chemnitz, and by *C. G. Haubold jr.,* Chemnitz.

As soon as the frame has been lowered into the vat it should be moved several times a few inches up and down in order to remove the small bubbles of air which adhere to the piece and might cause light spots. It is usual to enter the goods dry into the vat, but materials which do not readily become wet in the vat must be previously wetted out.

The flurry on the surface of the vat must be skimmed off with a piece of wood before entering or it will adhere to the piece and cause spots, this flurry is returned to the vat after dyeing in order to dissolve it up again. After the first dip the frame is screwed up a little to prevent the folds of cloth from touching, and to avoid unevenness the frame is reversed after each dip. Oxidation is brought about by hanging the piece for a short time over the vat letting it drip at the same time. If the piece has been freely hung on a frame the oxidation is assisted by beating the separate folds apart with a thin stick. The dips generally occupy 20—30 minutes for plain blues; heavy goods (linen and unions) which must be penetrated remain several hours, even over-night in the vat, goods printed with a resist only remain 10 minutes in the vat.

As in yarn dyeing, all unnecessary movement of the liquor during dyeing should be avoided in order to restrict as far as possible atmospheric oxidation and formation of flurry.

Continuous Vat.

The **roller vat** or **continuous vat** is employed for the dyeing of lighter calicoes, cretonnes, sateens, flannelettes, etc. Cloth printed with a resist can only be dyed in vats of this kind by a special method which will be described later (see chapter on resist printing). The continuous vat, as its name implies, differs from the dipping vat in that it works in a continuous manner and is capable on this account of a much greater production, it also requires less labour since the goods are drawn by mechanical means through the vat.

The construction of a continuous vat is seen from figures 4 and 5. The vats have generally two compartments or are arranged in sets of two with an average total volume of 290—370 cubic ft. The iron vat *A* (figure 4) is preferably sunk so far in the floor that its upper edge is at a convenient height for working. Instead of iron, vats may be constructed of cement, wood is not sufficiently durable, especially when vats are employed which contain caustic soda. In the figure *BB* are the rollers

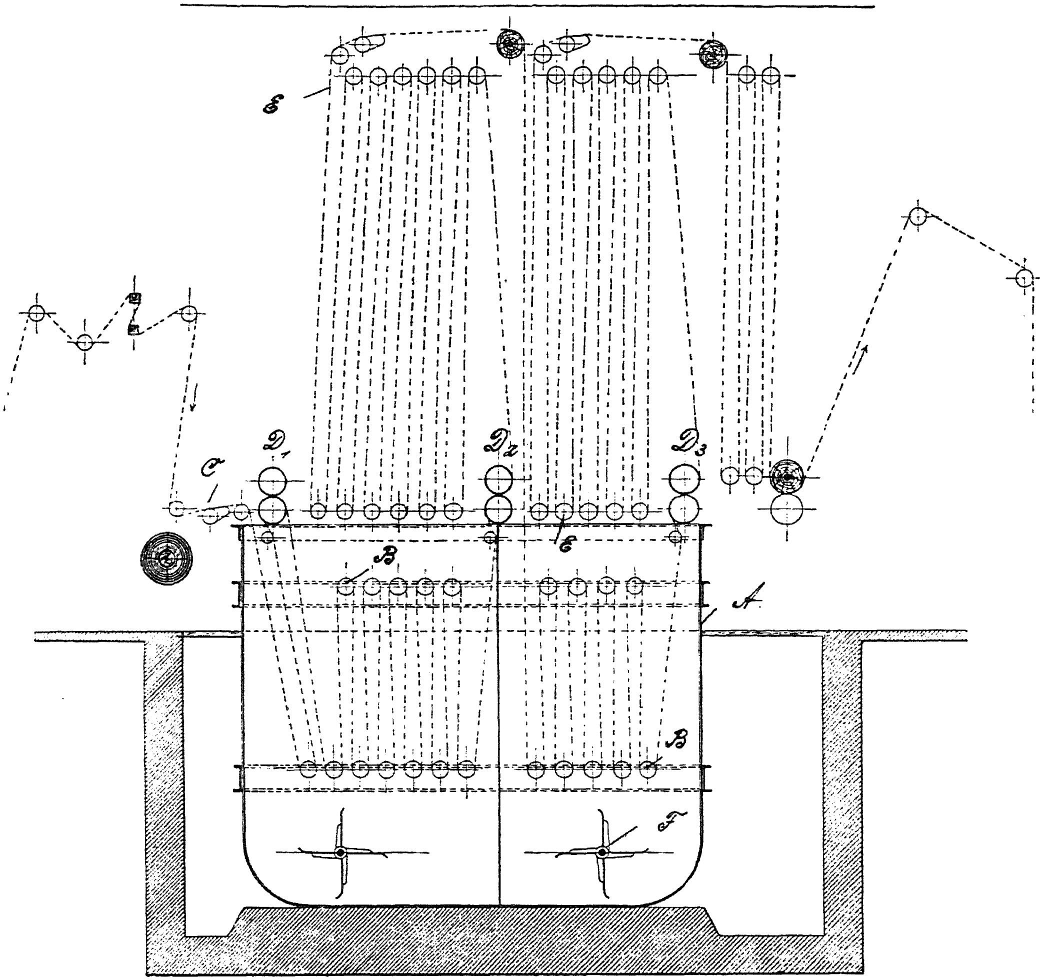


Fig. 4. Continuous Vat (for Zinc-lime Vat).

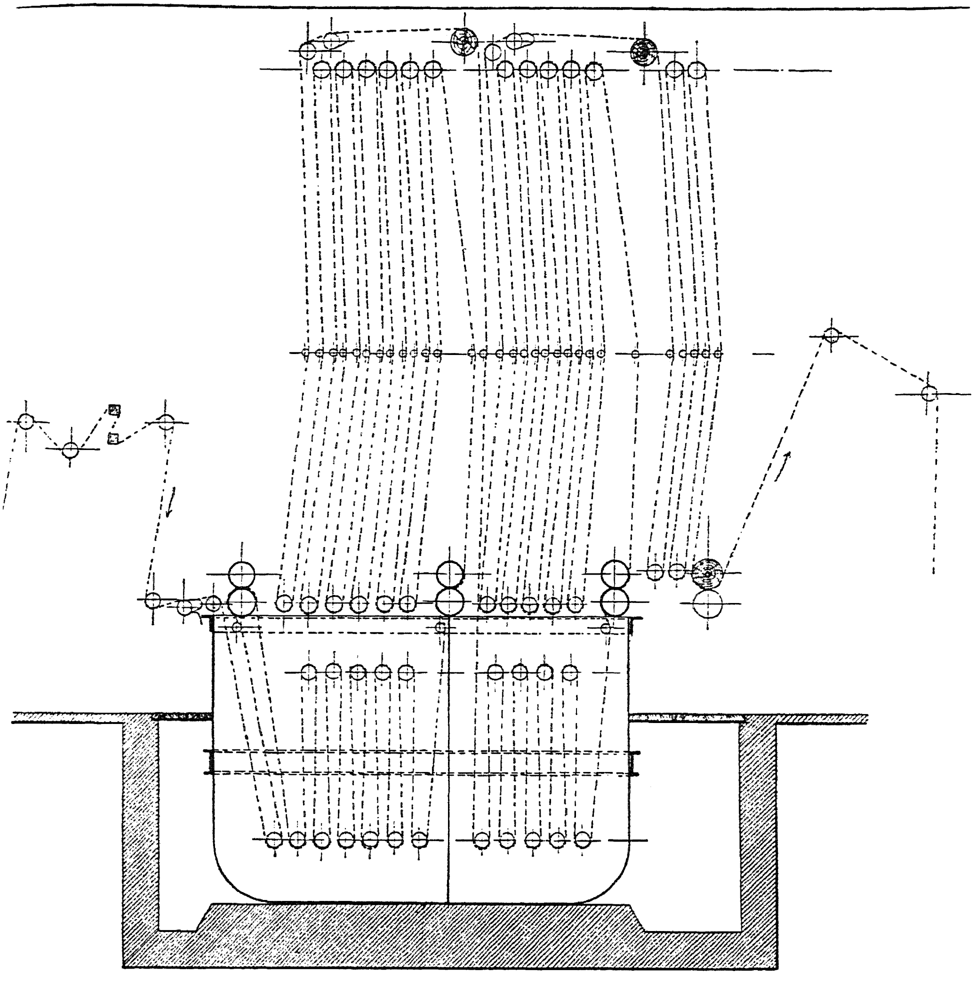


Fig. 5. Continuous Vat (for Hydrosulphite Vat).

made of copper or tinned iron which serve to guide the material through the vat. It is advisable to mount them on an iron frame which can be lifted out of the vat in case of any stoppage, such as tearing of the piece or guide bands, or for cleaning out the vat. *EE* are the guide rollers of the oxidising frame above the vat, these are also made of copper or tinned iron or they may be of wood.

The piece is drawn in the direction of the arrow over the scrimp rail *C*, and after passing once down and up again in the vat, it runs between squeezing rollers D^1, the so-called wetting-out rollers; these rollers are not absolutely necessary, but they greatly assist the penetration of the material by the liquor, which is particularly an advantage in dyeing pale shades. On leaving the first compartment of the vat the piece is squeezed by the rollers D^2 and oxidised on the frame above the vat. It is then given a second passage in the other half of the vat or in the vat next following, squeezed by the rollers D^3 and again oxidised in the air. To prevent the formation of folds it is advisable that the first, middle, and last roller of the oxidising frame should be expansion rollers. The squeezing rollers are made of iron, they have a diameter of about 8 in. and should be rubber-covered (this covering possesses the advantage over cloth wrappings that the goods are more evenly squeezed owing to the greater elasticity; it is also more durable). The pressure of the upper rollers on the lower rollers is regulated by means of screws or weights. A stirring arrangement is fixed in the lower part of the vat; this can be worked from the outside and is essential in the case of the vats which contain sediment for the purpose of thorough mixing when replenishing or springing the vat. For the hydrosulphite vat the stirrer is not indispensable, but it assists the thorough mixing in of the stock liquor and hydrosulphite added during the working of the vat and prevents any precipitated indigo from collecting on the bottom.

The depth of the vat and the height and length of the frame for the air passage are varied according as the clear hydrosulphite vat or the zinc-lime vat, which contains sediment, is employed. The zinc-lime vat requires a large space at the bottom of the vat for the collection of the gradually increasing sediment, the lower guide rollers must, therefore, be fixed about 18 in. above the bottom. The hydrosulphite vat on the other hand requires a higher and longer oxidising passage, so that the pieces, which oxidise more slowly on account of the dissolved hydrosulphite adhering to them, may be fully oxidised before passing into the next vat. The upper series of guide rollers is, therefore, placed 10—12 ft. above the lower series. The rate at which the pieces travel may be regulated at will by means of step-pulleys or bevelled gearing.

Dyeing in the Continuous Vat.

For the continuous vat, the hydrosulphite (or zinc-bisulphite) and the zinc-lime vats are most suitable. The clear hydrosulphite-soda vat, which contains no sediment, is always to be preferred, it is especially advantageous where the continuous vat is worked for the greatest possible production in a given time, since it can be kept continuously at the same strength and in a well-reduced condition by replenishing with dyestuff (stock-vat) and reducing agents. For this reason it is capable of turning out more work than the zinc-lime vat in which dyeing must be interrupted for the purposes of feeding and springing the vat. By the use of Hydrosulphite conc. powder, first introduced by the *Badische Anilin- & Soda-Fabrik,* especially in conjunction with Indigo solution, the hydrosulphite vat can be worked in a much more simple and reliable manner than was formerly the case. The production from a double vat containing about 1500 gallons worked with hydrosulphite and caustic soda is about 4200—5500 yards of a two-dip shade.

When dyeing in the continuous vat the goods are preferably entered dry, sateens, cretonnes, light raised goods and twills wet out readily and evenly in the vat, heavier materials, which are however but seldom dyed in the continuous vat, require a previous wetting out. Very thin, light materials have a tendency to crease in passing through the vat and, to avoid this, such goods may be stiffened with starch before dyeing, but it must be borne in mind that according to the amount of starch employed, the penetration will be more or less retarded. For every 100 gallons of water 1—10 lbs. of starch, previously made into a paste, should be taken; the goods are passed once lukewarm through this solution and dried. Indigo is taken up somewhat more rapidly by starched material, and the shade is more reddish in tone.

When the goods enter the vat dry the composition and volume of the vat-liquor can be regulated at will. The dry material will take a definite quantity of the liquor with it out of the vat and this allows of a continuous feeding of the vat with a stock-liquor without thereby increasing the volume; at the same time the accumulation of salts is retarded, an important factor in working the hydrosulphite vat. Replenishing during the working of the vat is carried out by introducing the stock-liquor at the bottom of the vat by means of a funnel with a long pipe. The strong liquor is distributed in the vat by the movement of the goods or better by a stirring arrangement.

The duration of a dip varies, but can be reckoned on the average as 2—2$^1/_2$ minutes, goods which are difficult to dye level are run more slowly, especially for pale shades. Care must be taken that the upper guiding rollers are always under the liquor, so that the pieces do not come in contact with the air. The surface of the liquor should as far as possible remain undisturbed as otherwise flurry is formed by oxidation and this becomes attached to the material causing stains. The squeezing of the goods after dyeing must be even, if unlevel dyeings are to be avoided, and the wrapping of the squeezing rollers must, therefore, be of an elastic nature.

Unlevelness in dyeing may easily be due to irregularity in the weaving of the goods, for instance, in the case of material of varying thicknesss the thinner places are less strongly squeezed by the rollers than the thicker places, they remain, therefore, more heavily loaded with liquor and appear in the finished dyeing as darker streaks.

White material should appear greenish yellow at the commencement of oxidation after the first dip and gradually change through green to blue. In the case of the zinc-lime vat the change takes place more quickly than with the hydrosulphite vat. If the piece on coming out of the vat for the first time appears greenish blue the vat is not sufficiently "sprung," *i. e.,* it does not contain enough reducing agent, but on the other hand it must not be so far reduced that the oxidation is not completed when the piece re-enters the vat, otherwise the unoxidised indigo white will be dissolved off again.

After dyeing the pieces are soured and washed when vats containing lime have been used, but in the case of the hydrosulphite vat they are merely rinsed and dried. Souring and rinsing are carried out in vats containing a series of rollers (similar to the dye-vats) and the waste acid or wash liquors are collected for recovery of the indigo (see page 102).

With regard to the influence of drying, calandering, etc., on the shade see pages 52 and 59.

As a rule the continuous vats are worked rather stronger than the dipping vats or those used in yarn dyeing, they contain most usually about 0·3 per cent. of indigotine. Variations above and below this figure naturally occur in special cases.

The zinc-lime vat is worked out ("blued-off") when the sediment accumulates to a disturbing extent or settles badly, giving rise to the danger of stains. Frequently the almost exhausted vats together with their sediment are transferred into dipping vats and there completely exhausted.

Hydrosulphite vats must be worked out when the salts have accumulated to too great an extent and tend to cause streaky dyeing. The liquor should not test above 15—18° Tw. Hydrosulphite conc. B. A. S. F. powder offers the advantage that it introduces less salts into the vat than hydrosulphite prepared on the spot.

Indigo R and G in the Dyeing of Piece-goods.

With regard to the employment of the special brands **Indigo pure R** and **Indigo pure G** in piece-dyeing the remarks apply which were made in reference to yarn dyeing. The *R* brand is chiefly of interest for plain blues only, since it is difficult to discharge in medium and dark shades.

Topping of the Piece-goods.

Pieces dyed in plain blue are in many cases, *e.g.*, linens, cotton and linen unions, twills, afterwards topped with aniline colours to impart brightness to the shade. This may be done either by topping in a special operation or in the finishing process. Colouring matters suitable for the purpose have already been mentioned on page 58.

9. Special Processes for the Treatment of Piece-goods before and after Dyeing.

In dealing with the subject of the preparation and after-treatment of piece-goods, reference may be made in the first instance to the

Influence of Mercerisation

which is of particular interest in piece dyeing.

It is well known that the mercerised fibre has an increased affinity for colouring matters, this is the case in a very marked degree with indigo and the fact must not be overlooked in dyeing. As a consequence of the rapidity with which the colour is taken up there is a tendency for mercerised goods to be insufficiently penetrated and unevenly dyed. For this reason care must be taken that the vats employed are not too strong, especially for the first dip. The shade obtained on mercerised cloth is brighter and more reddish than on ordinary cloth. Since indigo is not affected by alkalies, indigo dyed pieces can safely be mercerised after dyeing with the object of producing a silky lustre.

For piece dyeing those methods are of interest which effect in dark shades a saving of indigo or a deepening of the shade, and it is for these purposes that the methods of working now about to be described are employed.

Preparation of Piece-goods with Copper.*

Preparation of Piece-goods with Copper.

If a fabric is padded with a solution of copper sulphate and then dyed in the vat the indigo is taken up more rapidly than by unprepared material. One consequence of this rapid dyeing is a great tendency to unevenness. In pale and medium shades the tone is dull and greenish, dark shades have a blackish tone, the fastness to washing and soaping are normal.

The insufficient evenness of the dyeings may be obviated by the simple expedient of thickening the solution of the copper salt with starch. The process consists in padding with a starch paste containing 7 lbs. of starch and 5—10 lbs. of copper sulphate, according to the effect desired, per 100 gallons.

This process can be employed for discharge and resist prints, since the white is in neither case injuriously affected.

The other reactions of indigo (nitric acid spot, burning test) are not appreciably influenced by the preparation with copper.

Darkening of the Shade by Sizing and with Ferrous Sulphate.

Darkening of the Shade on Piece-goods by Sizing, etc.

The particulars given on page 57 regarding yarn dyeing apply also to piece-goods. The quantitative composition of the size depends upon the nature of the material and the degree of finish required.

---

* This method is old, it was first proposed by *D. Köchlin* (*Persoz,* Traité de l'impression III, 26).

For goods which have to be stiff and yet pliable, *e.g.*, linen apron materials, one part of tallow with two parts of starch is sufficient.

If it is desired to imitate the somewhat duller tone of vegetable indigo on light piece-goods (plain or with design) which have been dyed with Indigo pure it is sufficient to give a single passage through a bath at 120—140° F. containing 1 lb. starch and 1/2 lb. tallow per 1000 gallons, but to produce the black shade required for some "blue prints" the quantities of both starch and tallow must be one hundred times the above and after drying the operation must be repeated.

To increase the effect sulphate of iron (copperas) may be added to the size (see page 57).

Regarding the method of making the shade duller by a preparation or after-treatment with iron the remarks on pages 57 and 58 with respect to yarn dyeing hold good for pieces also. For discharge or resist prints a treatment with ferrous sulphate is inadmissible because the white would be dulled thereby.

Preparation of Piece-goods with Glue.

(Influence of glue on the dyeing of vegetable fibres.)

Influence of Glue on the Dyeing.

It was discovered some time ago by the *Badische Anilin- & Soda-Fabrik* (English Patent No. 12942 of 1897) that proteid substances (gelatine, glue, albumen, caseine, etc.) exercise a very considerable action on the dyeing of vegetable fibres. The most suitable of the above-mentioned substances is the ordinary bone glue or carpenters' glue. If a certain proportion of this is added to the vat, or even better if the material is prepared with it before dyeing, very bright, bloomy, and full shades result, such as are not to be obtained without the use of glue.

This beneficial action of glue is of special importance in piece dyeing, but may also be made use of in the dyeing of yarn.

The method of working is as follows:

Method of working in the Preparation with Glue.

The pieces are made ready for dyeing as usual and passed through a solution of 2 1/2—5 lbs. of glue in 100 gallons of water, then squeezed (*e.g.*, in a padding-machine) and dried before entering into the vat. Drying before dyeing gives rather better results than entering the goods wet, but, if this operation be considered to render the process too complicated, the treatment may be carried out by fixing in front of the continuous vat a small vessel fitted with rollers and containing the solution of glue. The pieces are run through this vessel, squeezed, and entered into the vat. In the case of dark blues, dyeings in 3 dips on glue-prepared cloth are equal in depth to ordinary 4-dip dyeings and show a brighter and redder shade. Dyeings produced by this process can be discharged in the ordinary way.

If glue-prepared and unprepared pieces are passed immediately after one another once or several times through the same vat a comparison of the results will clearly prove the beneficial action of the glue.

Adding the Glue to the Vat.

It is also possible to add the glue to the dye-vat, and in this case 20—30 % of glue, reckoned on the weight of pure dry indigo (not of the 20 % paste) in the vat should be taken, and after each addition to the vat of stock-liquor containing a known proportion of indigo a further 20—30 % of glue on the indigo contained in the stock-liquor is added in the form of a 10 per cent solution. Care must be taken that the glue solution be not added simultaneously with the stock-liquor, for if these two liquids are directly mixed the concentrated alkali may cause the glue to coagulate.

The above proportion of glue to pure indigo, which applies both to the preparation before dyeing and to the addition of glue to the vat is to be considered as approximately a fixed quantity, and it must be specially pointed out that an excess of glue will partially or wholly nullify the effect; beyond this it may be left to each dyer to find out for himself which method of employing the glue is best suited for individual cases.

Comparison of Glue-prepared and unprepared Dyeings.

The fixative property of the glue is made evident by the decreased amount of indigo removed from the fibre in rinsing and souring. The experiments described below were in every case so arranged that pieces of the same material with and without glue preparation were passed through one and the same vat immediately after one another — the unprepared piece always first. The glue-prepared piece came out under all circumstances much stronger, brighter, and redder in shade.

The estimation of indigo on the fibre was carried out by means of glacial acetic acid according to the method described on page 32.

The following table has a further interest inasmuch as it shows the relation of the amount of indigo lost in rinsing, etc., to the strength of the vat and to the number of dips, and thus illustrates the remarks on page 101.

All dyeings on bleached cretonne in the continuous vat.	**Indigo removed** (expressed in percentages of the total amount of indigo taken by the material from the vat)	
	without glue-prepare	**with glue-prepare**
A. Hydrosulphite-soda vat.		
Old exhausted vat:		
Medium blue in 4 dips* . .	17	13
Dark » » 8 » . .	10	9
Vat containing 0·266 % indigotine:		
Medium blue in 2 dips . .	39	28
Dark » » 4 » . .	24	21
Vat containing 0·133 % indigotine:		
Medium blue in 2 dips . .	31	24
» » » 4 » . .	33	27
B. Zinc-lime vat.		
Vat containing 0·2 % indigotine:		
Medium blue in 2 dips . .	38	33
Dark » » 4 » . .	30	22
Vat containing 0·1 % indigotine:		
Medium blue in 4 dips . .	26	11
Dark » » 8 » . .	20	14

The property possessed by glue of increasing the affinity of the fibre for indigo white is illustrated by the absolute amount of indigo taken up in the vat by the glue-prepared material. The experiments on this point have already been described in detail and are the same which furnished the results tabulated above with respect to the indigo removed by rinsing, etc.

---

* One dip means that the material is entered once into the vat, a passage through a continuous vat consisting of two compartments would be reckoned as two dips.

	Amount of Indigo on the material after rinsing or souring 100 parts of material (by weight) contain	
	without glue-prepare	**with glue-prepare**
A. Hydrosulphite-soda vat.		
Old exhausted vat:		
Medium blue in 4 dips . .	1 part	1·162 parts
Dark » » 8 » . .	1·76 parts	1·82 »
Vat containing 0·266 % indigotine:		
Medium blue in 2 dips . .	0·7 »	0·93 »
Dark » » 4 » . .	1·4 »	1·65 »
Vat containing 0·133 % indigotine:		
Medium blue in 4 dips . .	0·506 »	0·73 »
B. Zinc-lime vat.		
Vat containing 0·2 % indigotine:		
Medium blue in 2 dips . .	0·4 »	0·44 »
Dark » » 4 » . .	0·78 »	0·96 »
Vat containing 0·1 indigotine:		
Medium blue in 4 dips . .	0·5 »	0·69 »
Dark » » 8 » . .	0·9 »	1·16 »

It is thus evident that glue-prepared cloth exhausts the vat more rapidly and fixes the indigo more firmly. The larger proportion of indigo on the cloth corresponds to the deeper, fuller shade.

10. The Dyeing of Cops and Cheeses.

The Dyeing of Cops and Cheeses.

The advantages offered by dyeing cotton in the form of cops or cheeses compared with dyeing in the hank have been turned to account in connection with vat dyeing, and there are now several forms of cop-dyeing machine in use, some of very ingenious construction, which admirably serve their purpose.

It must first of all be emphasised that the construction of the apparatus must be adapted to the properties of the indigo vat and the method of employing it in dyeing. Most of the cop-dyeing machines which are to be found working may give excellent results with other colouring matters, but for the reason just mentioned they are unsuitable for the rational application of indigo. Experiments have frequently been carried out with unsuitable machines and with insufficient knowledge of the working of indigo vats, and these have naturally led to an unfavourable judgment regarding the dyeing of cops with indigo; the dyer must, therefore, have an exact knowledge both of the behaviour of the vat and of the construction of the machine.

The conditions which must be fulfilled by a machine for dyeing cops with indigo are in our opinion the following:

The vat liquor, while circulating through the cops and cheeses, must be maintained at a **constant level** and must come as little as possible into contact with air, that is to say, only the unavoidable contact at the surface of the vat should take place. The liquor may be circulated in either direction alternately or only by suction from the outside to the inside; experience has shown that the latter method suffices. Machines in which the level of the liquor varies should be avoided.

The removal of superfluous liquor by suction and the oxidation of the vat liquor in the cops must take place in the machine itself or at any rate on the cops-carrier immediately after leaving the vat. The method of oxidising in the hydro-extractor may be considered as obsolete.

Fixing the cops or cheeses on perforated spindles is to be preferred to packing them tightly in blocks, the latter method is less reliable and renders the oxidation more difficult. The cops must remain on the same spindles from the commencement of the process until the completion of the dyeing operation.

It is indispensable that the spinner should supply the cops in good and regular quality, otherwise even in the best machine a certain amount of waste will result.

It is very advantageous although not absolutely necessary to remove all the air from the wetted-out cops before they enter the dye-bath; there is then no danger that the vat liquor as it penetrates the cops will encounter oxygen, which would cause premature precipitation of indigo.

The most important points in cop-dyeing are the removal of the vat liquor from the cops after dyeing and the oxidation. Both operations should take place by means of **suction,** *i. e.,* air should be drawn from the exterior inwards and not forced through the material. The more quickly these operations are performed, the better and more even will be the dyeing. In the first stage of this suction the superfluous liquor is removed, in the second the air brings about oxidation.

In the dyeing of cops, as in all other cases where dyeing takes place by circulation of the vat liquor, the hydrosulphite vat should be employed. This method of dyeing has been greatly simplified by the introduction of the two products: Hydrosulphite conc. B. A. S. F. powder, first brought into the market by the *Badische Anilin- & Soda-Fabrik,* and Indigo solution B. A. S. F., and the employment of these products goes far to ensure a safe and exact working. The vat is set and worked according to the instructions given on page 84, the process being simplest when Indigo solution B. A. S. F. is used. Satisfactory dyeings will only result when the vat is clear and completely reduced, containing the dyestuff in perfect solution; if the colouring matter even only partially should separate out in a solid form the cops or cheeses will act as a filter. In this case the outer layers of yarn will be dyed through and will also be soiled with the precipitated dyestuff, whilst the inner layers will come only slightly or not at all into contact with the vat liquor. For a similar reason the water employed should be as soft as possible (condensation or river water), otherwise the caustic soda in the vat will precipitate the substances in the water, and this precipitate will be filtered out on the cops, which will thus be soiled. The stock vat must be perfectly clear before use, and this may be ensured either by allowing it to settle and drawing off the clear liquor by means of a pipe inserted some distance above the bottom of the vessel and bent upwards, or still better by filtering it through a filter-press, which affords the surest guarantee for the absence of a precipitate.

Of the various machines now on the market the following have been found by practical experience to be suitable for indigo dyeing; the so-called "revolver" dyeing machine made by *Krantz* of Aachen, and the *Grämiger* machine (rotation machine), which both fulfil the requirements detailed above and are best suited for indigo dyeing, and the *Thies* machine.

We now give a description with sketches of the

Indigo Revolver Dyeing Machine

(supplied by *Krantz*, Aachen).

In the figures 6 and 6a, *C* is a disc revolving on its axle *B* and mounted in the vessel *A* in such a way that two of its four openings *D* are always in the liquor and two out of it. By means of screws *F*, perforated cops-carriers *E* are tightly fixed into these openings. Under the liquor the suction and pressure pipe *G* of the pump *H*, and above the surface of the liquor the pipe *I* from the vacuum chamber and air pump *K* connect with the cops-carriers through the openings in the disc.

The method of working is as follows: — Suppose the disc revolves in the direction of the hands of a clock, the carrier holding the cops or cheeses is tightly fixed by means of the screw *F* in the right-hand opening of the disc (when out of the liquor). By pressing on a lever the disc is revolved through an angle of 90°, so that the carrier is connected with the suction pipe of the pump. As can be seen from the sketch the carrier is inclined at an angle, so that when entered into the vat the air escapes from the perforated tubes and the cop spindles. The liquor is drawn through the cops for 1 1/2 — 2 minutes, and during this time a second cops-carrier is inserted in the upper right-hand opening of the disc, which is then again turned through an angle of 90°, so that the first carrier is now opposite the pressure pipe of the pump and the second opposite the suction pipe. The disc remains in this position 1 1/2 — 2 minutes, during which time a third carrier is inserted. A further revolution through 90° takes place, and now the first carrier, through which the liquor has been both drawn and forced, is connected to the air pump, and by means of powerful air current the material is freed from the adhering liquor and oxidised.

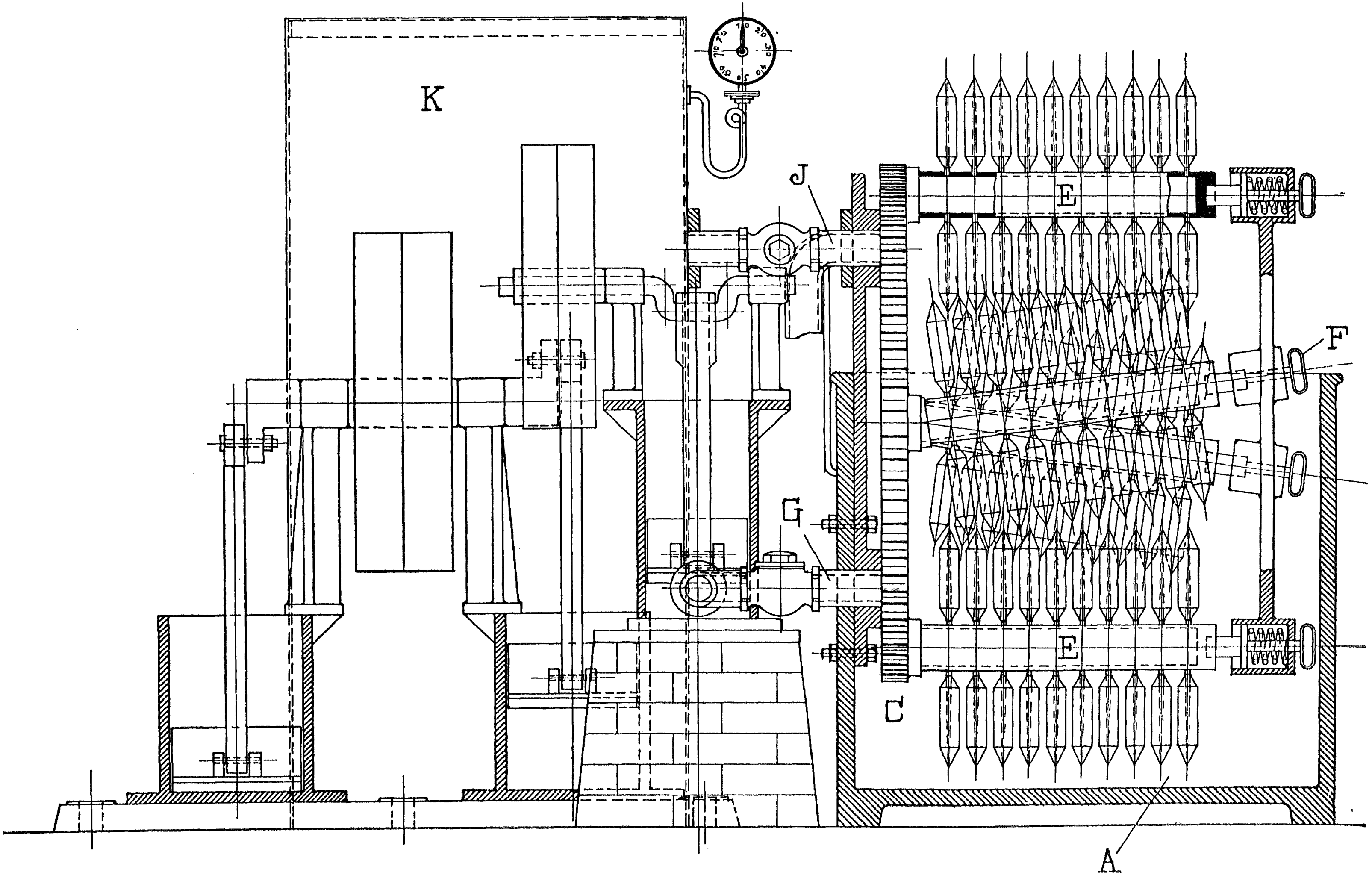


Fig. 6. Indigo Revolver Dyeing Machine by Krantz, Aix-la-Chapelle. (Vertical Section.)

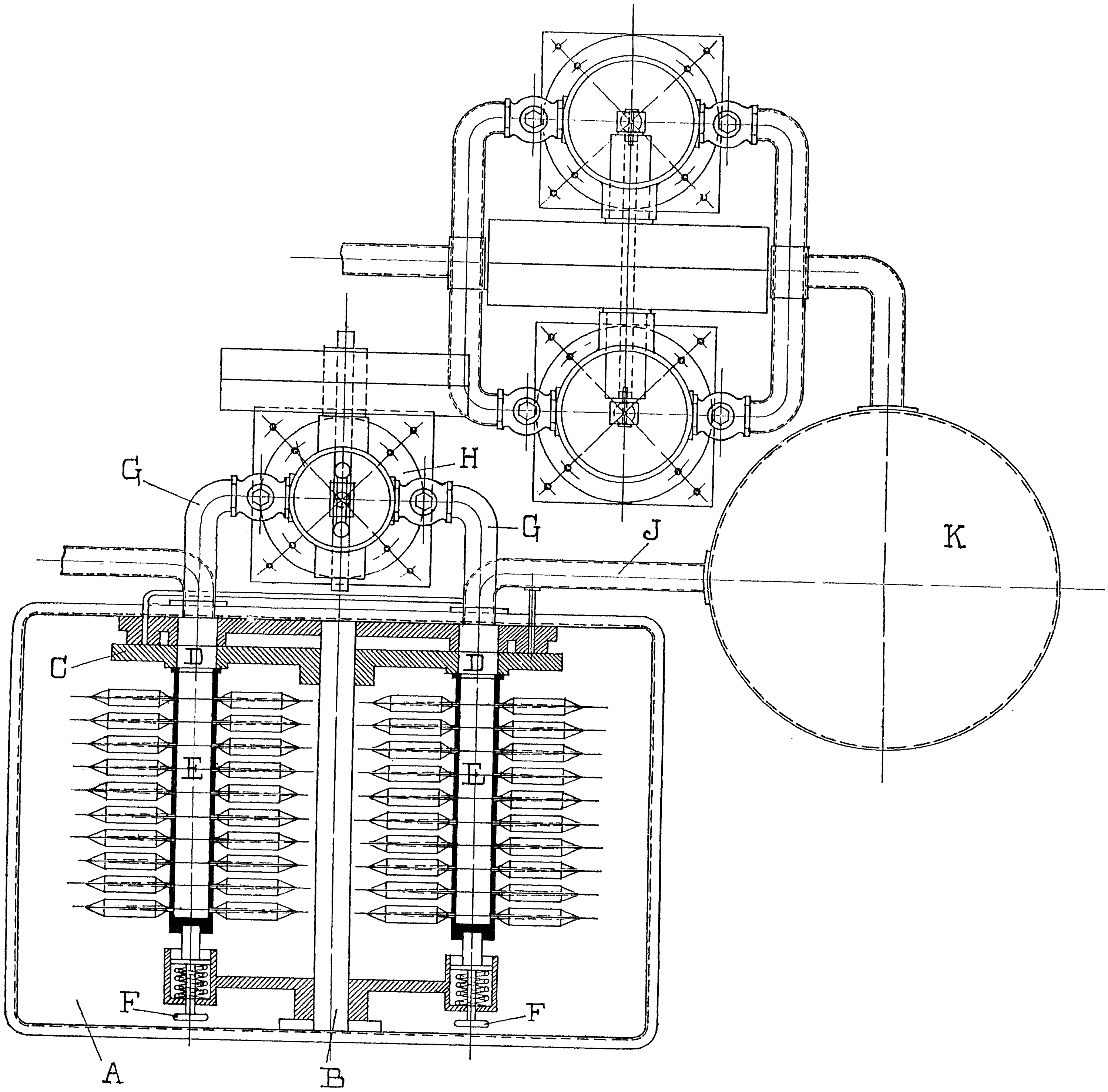


Fig. 6a. Indigo Revolver Dyeing Machine by Krantz, Aix-la-Chapelle. (Horizontal Section.)

Owing to the slanting position of the cops-carriers already referred to, the liquor in them runs off when they leave the vat.

The disc is once more turned through an angle of 90° when the first carrier returns to its original position, where it is taken off and replaced by another carrier freshly filled with cops.

The process is thus continuous, the liquor is both sucked and driven through the material, and the removal of the superfluous vat liquor takes place immediately on leaving the dye-bath. The vat is continuously and automatically fed with liquor from the stock vat, and the concentration in this way remains always the same.

The manipulation is simple, since nothing need be done by hand beyond fixing the cops on the carriers and putting in and taking out the carriers. The apparatus is capable of dyeing about 1750 lbs. of cops or cheeses in a working day of 10 hours.

A simple arrangement consisting of a vessel in which water is driven or sucked through the cops serves for wetting out the cops before dyeing and rinsing the dyed material.

11. The Dyeing of loose Cotton and Sliver.

It is not economical to dye cotton with indigo before spinning since the loose fibre takes up a disproportionate amount of colouring matter.

Loose Cotton.

Loose cotton absorbs about seven times its own weight of liquor, which must be removed by hydro-extracting or squeezing, involving a considerable oxidation, and, therefore, large quantities of reducing agent are used up. The hydrosulphite-soda vat and the zinc-lime vat are not very suitable for dyeing loose materials. To produce medium and dark shades several dips would be necessary; but through this process the cotton loses in spinning properties. The best process is the hydrosulphite-ammonia vat, in which a medium shade of blue of normal fastness may be dyed in one dip only.

Dyeing is carried out in either a dipping basket or a net, squeezing the material after each dip, or in a machine (such as the *Obermaier*) with a circulating liquor. In the former case the cotton must be very carefully handled or it will cake together in lumps and cause loss in spinning.

In machine dyeing the loose cotton must be evenly and tightly packed in order that the liquor may penetrate all parts of the material. Immediately after dyeing the material must be hydro-extracted, the liquor coming from it being retained for further use.

Sliver. The disadvantages mentioned in connection with dyeing loose cotton are less apparent in the case of sliver, but on account of the large quantity of dyestuff required, this method is only to be recommended for light shades. Dyeing takes place in the same manner as with warps, several bands of material are run parallel through the vat over guide rollers, then squeezed and oxidised. Tearing of the bands is prevented by carrying them through the machine on perforated rubber cloths.

12. The various kinds of Vat employed for dyeing Cotton and other Vegetable Fibres.

a) Zinc-lime Vat.

Zinc-lime Vat. The working of the zinc-lime vat depends upon the property of zinc dust to react with slaked lime, forming calcium zincate and hydrogen.

$$Zn + Ca(OH)_2 = Zn\,O_2\,Ca + H_2.$$

The hydrogen thus liberated reduces the indigo to indigo white which dissolves in the excess of lime present.

Beyond this the process of reduction in the zinc-lime vat does not appear to be so simple, many things indicate that the chemical process taking place is of a complicated nature.*

It is of importance that the indigo in the zinc-lime vat should be in as finely divided a condition as possible, if coarse particles of colouring matter are present they escape reduction and remain undissolved in the vat sediment.

---

* See *Binz* and *Rung,* Die Zinkstaub-Küpe, Zeitschrift für angewandte Chemie 1899, No. 21 and 22, and *Binz,* Zeitschr. für Elektrochemie, 1898, No. 1 and 9.

Brands of Indigo for the Zinc-lime Vat.

The various paste brands of Indigo pure are delivered ready for use in this vat, *viz.:*

Indigo pure B. A. S. F. paste 20% SB,
» » » paste 20% S,
» » » paste 40% S,
» » » paste 20%,
» » » paste 30%.

The following powder brands,

Indigo pure B. A. S. F. powder SL,
» » » powder L,

only require to be previously made into a paste (as directed on pages 82—84) and the paste then passed through a sieve. The following brands,

Indigo pure B. A. S. F. powder S,
» » » powder,
» » » in pieces S,
» » » in pieces,

must, however, be wet ground in the ordinary indigo mill.

The *R* and *G* brands may also be used in the zinc-lime vat.

Setting the Vat.

In setting the vat care must first be taken that the quantities of lime and zinc dust will suffice for complete reduction of the indigo but are not unnecessarily large; the vat sediment, which in any case will increase as the vat is worked, owing to the repeated addition of stock vat, should be as small as possible at the commencement.

This small amount of sediment distinguishes the zinc-lime vat to its advantage from the copperas vat, which contains five times the quantity of sediment.

By careful investigation and practical experience it has been found that it is not rational to carry out the reduction of the indigo, as was formerly done, in the cold or directly in the dye-vat. By working in this manner not only is more time necessary to bring the indigo into solution, but there is also a danger of loss of colouring matter owing to incomplete reduction or to a portion of the dyestuff remaining undissolved in the dye-vat. Besides this, the sediment settles much more slowly than when a stock vat is prepared.

It is, therefore, advisable to set a stock vat, and for this purpose a suitable vessel with as small a surface area as possible, *e. g.,* a cask with a well-fitting lid, should be taken. The stock vat should contain 125 lbs. Indigo paste 20 % or 25 lbs. of powder per 100 gallons. The complete reduction of the indigo will take 4—6 hours at a temperature of about 120° F.; long standing is detrimental, and for this reason the stock vat should not be prepared in sufficient quantity for continued use, but should be set afresh when required. The greater yield of indigo is ample recompense for the additional trouble.

Loss in the Vat.

The loss arising from allowing the stock vat to stand too long or from reducing in the cold, which amounts to the same thing, may amount to about 20 % of the amount of indigo (calculated on pure colouring matter), whereas a warm and rapid reduction does not involve a loss of more than 8—12 %. It may be mentioned for comparison that in the case of the copperas vat a loss of 20—25 % is regarded as normal. Excessive quantities of zinc dust or too high a temperature in setting the stock vat are other possible causes of loss.

Care must be taken that only fresh lime, free from stones and sand, and good dry zinc dust are taken; should the latter contain lumps it is of little value for the purpose.

Stock Vat.

Example of the setting of a Stock Vat.

20	lbs.	Indigo paste 20 % SB or a corresponding quantity of some other *S* brand are mixed with
2 1/2	»	zinc dust previously made into a paste with 4 gallons water at 120—140° F., and to this mixture while still warm are added
8-10	»	quicklime previously slaked to an even paste.

The mixture is made up to 16—20 gallons with hot water, and this stock vat, which should have a temperature of 120—140° F., is well stirred at intervals. In about 5 hours the mixture has a pure yellow colour and is ready for adding to the dye-vat.

The *R* and *G* brands are treated in the same way.

Preparation of the Dye-vat.

Dye-vat.

In setting a fresh vat it must be borne in mind that the water of the dye-vat contains in solution atmospheric oxygen, which has the power of precipitating indigo from the vat. In order to counteract this effect additions of zinc and lime are made to the dye-vat a few hours before the stock vat is poured in. The quantities of these substances to be added vary; when setting weak vats more zinc and lime are required than for strong vats; on an average $^1/_4$ lb. zinc dust and about 1 lb. of quicklime previously slaked per 100 gallons of vat liquor are taken.

When the necessary quantity of the stock vat has been added to the dye-vat the latter is thoroughly well stirred and allowed to settle, it is then ready for dyeing to be commenced.

It is a peculiar property of the zinc-lime vat that, especially soon after it has been set, the presence of unaltered zinc dust and lime in the sediment gives rise to an evolution of hydrogen gas which forces up a part of the sediment to the surface of the vat. To prevent this occurring during dyeing with consequent soiling of the material, the vat is stirred up regularly before commencing work, so that the gas formed in the sediment is liberated, and is then allowed to settle again.

The vat liquor and also the sediment must always show a yellow colour; if the liquor through continued use becomes greenish the vat must be again "sprung." Hard and fast rules as to the quantity of reducing agent required for springing the vat cannot be given. To a vat containing 100 gallons may be added in the evening according to the appearance of the liquor $^1/_2$ — 1 lb. lime and $^1/_4$ — $^1/_2$ lb. zinc dust.

The vat ought not to be allowed to become too cold in winter, a temperature of 65 — 70° F. — *i. e.,* about the normal summer temperature — is most favourable.

b) The Copperas Vat.

Copperas Vat.

In this vat ferrous sulphate (copperas) and slaked lime are employed as reducing agents. The chemistry of the process is shown by the following equations:

$$Fe\,SO_4 + Ca\,(OH)_2 = Fe\,(OH)_2 + Ca\,SO_4.$$

The reducing agent is the ferrous hydrate formed by the above reaction, which reduces the indigo and is itself converted into ferric hydrate

$$2\,Fe(OH)_2 + 2\,H_2O + C_{16}H_{10}N_2O_2 = Fe_2(OH)_6 + C_{16}H_{12}N_2O_2.$$

The indigo white formed in this way is held in solution as a calcium salt by the excess of lime in the vat.

Brands of Indigo for the Copperas Vat.

We recommend the following brands for the copperas vat:

Indigo pure B. A. S. F. paste 20 %,
» » » paste 30 %,

which are ready for use as supplied, also

Indigo pure B. A. S. F. powder L,
» » » powder,
» » » pieces,

which, as in the case with the zinc-lime vat, must previously be made into a paste or ground wet.

Setting the Vat.

To set a vat a concentrated stock vat is first prepared which serves to feed the dye-vat. In preparing the stock vat care must be taken that an excess of ferrous sulphate is not employed, that the temperature does not rise too high, and that the stock vat does not remain standing too long before it is added to the dye-vat. If these precautions are not observed, the loss of dyestuff, in any case unavoidable, is much increased.

Loss in the Vat.

The copperas-lime reduction always results in a considerable loss of dyestuff. Under the most favourable conditions 75—80 % of the indigo taken may be found in the dye-vat, it is very seldom that the loss falls below 20 %. A portion of the indigo may be found in the form of an insoluble compound (probably in combination with iron) in the vat sediment and can be recovered by a treatment with hydrochloric acid followed by filtration and reduction. The value of the indigo so obtained would not pay for its recovery, and the process is, therefore, not of practical interest.

A further disadvantage of the copperas vat is the large quantity of sediment, about five times as much as in the zinc-lime vat. This renders a replenishment of the vat impossible or nearly so.

Examples of the preparation of Stock Vats.

Strong Vat.

30 lbs. Indigo pure B. A. S. F. paste 20 $^0/_0$ are mixed with about 6 gallons water at 140° F. Add to this warm mixture a smooth thin paste made by slaking

36 » quicklime and then add with constant stirring a solution of

24 » ferrous sulphate in about 10 gallons of hot water (120—140° F.) and make the whole up to 50—60 gallons with water.

The stock vat is best prepared in a cask with a lid. The mixture should be covered up and allowed to stand with occasional stirring for 4—6 hours and should then be quite yellow with a fine coppery flurry.

Medium Vat.

16	lbs.	Indigo pure B. A. S. F. paste 20 $^0/_0$	about 36 gallons water.
16	»	ferrous sulphate	
20	»	lime	

Weak Vat.

8	lbs.	Indigo pure B. A. S. F. paste 20 $^0/_0$	about 18 gallons water.
10	»	ferrous sulphate	
12	»	lime	

These are prepared in the same way as the strong vat. The copperas and quicklime must always be fresh.

Preparation of the Dye-vat.

Dye-Vat.

As with the zinc-lime vat an addition of reducing agents must be made to the dye-vat some time before the stock vat is poured in; for every 100 gallons of liquor

1 lb. ferrous sulphate
1 $^1/_2$ lbs. quicklime

are taken.

The dye-vat is about two-thirds filled with water and the stock vat added. After stirring up and allowing to settle dyeing may be commenced.

The copperas vat is usually not replenished, it is used 3 times a day, 50 lbs. yarn being dyed each time, and each time after use it is well raked up. The vat is exhausted after 26—28 rounds have been dyed, *i. e.,* in about 10 days.

The copperas vat must always be allowed to settle perfectly before dyeing is commenced. If dyeing takes place in vats which are not clear, the finely divided ferrous or ferric hydrate is deposited on the fibre, and the shade of the dyeing is very unfavourably affected.

The vat liquor and the sediment must always have a yellow colour; if they become green on continued dyeing and the normal colour does not return on allowing the vat to stand, the vat must be sprung by an addition of copperas, which must be regulated according to the colour of the vat. As a rule it is sufficient to dissolve a few pounds of copperas in water and stir the solution into the vat. If the vat after standing for some hours or over-night still does not show the normal appearance, it must be sprung again.

The vat must not be worked too cold in winter, a temperature of 65—70° F. is most favourable.

Directions for making Indigo pure powder into paste.

Preparation of a paste from Indigo L.

1. Preparation of a paste from Indigo pure B. A. S. F. powder L by means of a solution of glue.

To make into a paste

20 lbs.	Indigo pure B. A. S. F. powder L dissolve
2 oz.	joiner's glue in
2 gall.	boiling water, and when dissolved add
$^1/_6$ pint	caustic soda 76° Tw. To this solution, which is best contained in a 20 gallon cask, now add
4 lbs.	Indigo pure B. A. S. F. powder L.

Then slowly press down the indigo powder floating on the surface with a perforated dasher similar to the butterstaff used for churning. The powder is at once moistened and by pressing down slowly at first and continuing the pressure for some time it is completely stirred in. Having then added

3 gall. boiling water, stir well and add a further

8 lbs. Indigo pure B. A. S. F. powder L, moisten this by stirring up several times and add another

3 gall. boiling water. After stirring again add the last

8 lbs. Indigo pure B. A. S. F. powder L and mix it in by stirring for a short time.

By vigorous and continuous stirring for at least half an hour a 20 % indigo paste is obtained which can then be diluted with water to any desired consistency.

2. Preparation of a paste by means of steam.

20 lbs. Indigo pure B. A. S. F. powder L are mixed in a cask with

10—20 gall. of hot water.

Then pass a current of steam into the water — not into the indigo powder floating on the surface, as this would fly off like dust — until the whole mass is boiling up vigorously. Then stir thoroughly in order to bring the indigo into intimate contact with the boiling liquid. In a short time the indigo is moistened and forms a thin paste which can be used for setting a vat.

The indigo is not injuriously affected by the process of boiling.

3. Preparation of a paste from Indigo pure B. A. S. F. powder SL.

Preparation of a paste from Indigo SL.

Our Indigo powder SL has the property of forming with extraordinary ease, when stirred up with hot water, a smooth paste which does not settle out even on long standing, and this can be readily and completely dissolved in any kind of vat, notably in the fermentation vat, without further wet grinding.

The simplest method of working is first to pour the necessary quantity of boiling water into a cask, or other vessel of similar shape, then put in the indigo powder and close the vessel tightly with a well-fitting lid with the aid of cloths if necessary.

The steam which rises moistens the indigo, so that it loses its tendency to fly about like dust, part of it sinks readily, and after about 10—15 minutes the remainder can be easily mixed with the liquid by stirring for a short time with a broom of twigs or a wooden stirrer.

The paste is ready for use after it has been stirred for several minutes in order to attain the most even consistency possible.

For a vessel of the size of a petroleum cask, for example, 20 lbs. of Indigo pure powder SL may be made into a paste with about 10 gallons of hot water.

c) The Hydrosulphite-soda Vat.

Hydrosulphite-soda Vat.

The working of this vat has been rendered much simpler and easier by the introduction of

Hydrosulphite conc. B.A.S.F. powder,

which we were the first to place on the market.

Hydrosulphite conc. B.A.S.F. powder.

This powder possesses the great advantage over all previously known commercial hydrosulphites of being much more concentrated and at the same time perfectly stable. Hydrosulphite in solution, as is well known, is an unreliable product, since its effective value diminishes or entirely disappears on standing owing to decomposition. Hydrosulphite in powder on the contrary allows of a simple and convenient method of working, since it need not be previously dissolved, but may be added direct in the form of powder when setting the stock vat or springing the dye-vat.

In setting a vat Hydrosulphite conc. B.A.S.F. powder is used to the greatest advantage without previous solution, for in this way its reducing action comes most powerfully into play. It dissolves readily in the vat when slowly strewn in and the vat well stirred, the portions added at one time must not be too large or lumps may be formed which only dissolve with difficulty.

It is very important that the powder should be stored in vessels which are protected from moisture and from great heat, and that the scoops, etc., used for taking it out are perfectly dry.

In working continuous vats a solution of the hydrosulphite may be employed with advantage for springing the vat, since the more rapid and equal distribution of the solution will favour the smooth and continuous working of the vat.

Preparation of a Solution of Hydrosulphite from Hydrosulphite conc. B.A.S.F. powder.

Solution of Hydrosulphite from Hydrosulphite conc. powder.

Cold water must always be used for the solution. The solution must not be prepared in large quantities, but only in amount sufficient for one or two days' work, because on standing it loses in reducing power, especially in warm weather. The hydrosulphite is dissolved in a cask with a well-fitting lid, and the following proportions and order of addition must be closely adhered to.

Add to 10 gallons cold water

1 gall.	caustic soda 42° Tw. (or 1/2 gallon at 76° Tw.) and
20 lbs.	Hydrosulphite conc. B.A.S.F. powder. The powder is added in small portions at a time with constant stirring.

When solution is complete add a dessertspoonful of indigo (paste or powder). Any unnecessary stirring, transference from one vessel to another, or other disturbance of the solution should be avoided, nor should the vessel containing it be left uncovered.

The following simple method of testing by means of "Indigo carmine for titration" serves to indicate whether the hydrosulphite solution has retained its reducing power.

Testing the Solution of Hydrosulphite.

4 grms. "Indigo carmine for titration" (corresponding to exactly 2 grms. indigo) are dissolved in 1 litre of water. 250 c.c. of this solution (corresponding to 0·5 grm. Indigo pure) are poured into a glass flask of about 400 c.c. capacity. The hydrosulphite solution is then run into the flask from a pipette, a drop

at a time, as regularly as possible but not too slowly, the flask being continuously shaken with a regular motion. When the blue colour of the solution disappears and suddenly changes to pale yellow the reaction is complete.

The best method is to agitate the flask with one hand, holding the pipette in the other and closing it above with the forefinger. In any case the test must always be carried out in exactly the same manner, and two successive valuations of the same hydrosulphite solution must give like results.

Since the amount of the colouring matter used for the titration corresponds to 0·5 grm. Indigo pure, double the number of the c.c. of hydrosulphite required will indicate how many c.c. would reduce 1 grm., or how many litres reduce 1 kilo, or how many gallons reduce 10 lbs. of indigo.

The figure thus obtained by doubling the result directly obtained, the so-called "titre" of the hydrosulphite solution, should be 4 or at the most 4·5 in the case of a solution freshly prepared according to the directions given above; if it is higher, correspondingly more hydrosulphite solution must be taken for springing the vat.

Brands of Indigo for the Hydrosulphite Vat.

The following brands of indigo are employed for the hydrosulphite vat:

Indigo pure B.A.S.F. paste 20 %,
» » » paste 30 %,
Indigo solution B.A.S.F. 20 % for cotton,
Indigo vat B.A.S.F. 60 %,
Indigo pure B.A.S.F. powder L,
» » » powder,
» » » pieces,

and also the *R* and *G* brands.

Hydrosulphite Vat in general.

In contradistinction to the zinc-lime and copperas-lime vats, in which the reducing agent is present in the sediment and only becomes effective when brought into contact with the indigo by stirring, in the hydrosulphite vat the liquid itself, *i. e.,* the dissolved hydrosulphite, is the reducing agent.

This solution immediately surrounds the particles of indigo, and for this reason the hydrosulphite reduces more rapidly than zinc dust or ferrous sulphate, the hydrosulphite vat is, therefore, ready for dyeing much sooner after setting than the other vats. Similarly in springing the vat the added hydrosulphite has a more rapid action than, for example, the insoluble zinc powder which has first to react with the lime in the vat.

Besides this advantage, to which is due the greater dyeing capacity of the hydrosulphite vat compared with other forms of vat, hydrosulphite possesses the valuable property of not exercising any destructive action on the colouring matter. Even when used in excess it does not destroy indigo by over-reduction; the loss of indigo is not above 1—2 $^0/_0$, and in strongly reduced vats without flurry or with very little flurry the loss falls to 0·5 $^0/_0$.*

If we now compare this with the other cotton vats we find that experience shows the loss of indigo under normal conditions to be

in the copperas vat . . . 20—25 $^0/_0$,
» » zinc-lime » . . . about 10 $^0/_0$,
» » bisulphite-zinc vat . » 5 $^0/_0$.

In the two last named vats the loss through destruction of indigo may be much greater than this owing to the stock vat standing too long or the temperature rising too high.

A further advantage of the hydrosulphite-soda vat is the absence of sediment. For this reason it is not necessary to empty the vat so frequently, whereby saving of labour is effected and an increased output results. The omission of the souring operation, necessary in the case of material dyed in the zinc-lime and copperas vats, also reduces the amount of labour.

The hydrosulphite vat yields dyeings which in the case of medium blues are somewhat less reddish in tone and dark shades which are deeper and less coppery than those dyed in the zinc-lime and copperas vats. These differences are intensified when the amounts of caustic soda and hydrosulphite in the hydrosulphite vat are increased.

In setting a hydrosulphite vat a stock vat is first prepared, and this is used for setting and replenishing the dye-vats.

---

* Compare also *Binz* and *Rung,* Ausnützung des Indigos in der Hydrosulfitküpe. Zeitschrift für angewandte Chemie, 1898, No. 42.

Stock Vat with Indigo pure.

Example of the preparation of a Stock Vat with Indigo pure B. A. S. F.

Stir

100 lbs.	Indigo pure 20 % (or 20 lbs. powder or pieces made into a paste) in a wooden cask provided with an open steam pipe with
20 gall.	hot or cold water and
6 »	caustic soda 76° Tw. or 12 gallons at 42° Tw. When thoroughly mixed add in small portions with constant stirring
17 lbs.	Hydrosulphite conc. B. A. S. F. powder and mix by thorough stirring, but avoid stirring too much air into the mixture. At the same time raise the temperature by means of steam to about 110° F.

The above proportions hold good for both weak and strong vats of the concentration usually employed for piece-goods. For setting very weak vats (such, *e. g.*, as are used for pale "pearl" shades on yarn) the proportion of caustic soda may be increased by one-half or at the most doubled.

The warm stock vat is allowed to stand until completely reduced. This is shown by the mixture running off clear and yellow from a strip of glass dipped into it and requiring 25—30 seconds for oxidation. If correctly prepared a vat set with the above proportions should be reduced completely in half an hour. If the test with the glass shows that the vat is not yet pure yellow or oxidises too quickly, further small portions of hydrosulphite are stirred in and the test repeated after 10—15 minutes.

The fact must not be lost sight of that vats which are too fully reduced (*i. e.*, which contain too much hydrosulphite and, therefore, oxidise very slowly) will not yield deep shades, because under certain conditions they dissolve off a part of the indigo from the fibre.

The preparation of the vat may be simplified by the use of Indigo solution B. A. S. F. 20 % for cotton, which contains the indigo already reduced and in solution.

Preparation of a Stock Vat with Indigo solution B. A. S. F. 20 % for Cotton.

Stock Vat with Indigo Solution.

9 gall.	(or 100 lbs.) Indigo solution B. A. S. F. 20 % are stirred up in a wooden cask with
4 »	caustic soda 76° Tw. or 8 gallons at 42° Tw.* and
20 »	hot water.
6 lbs.	Hydrosulphite conc. B. A. S. F. powder are then added in small portions at a time with constant stirring.

The further details are exactly as given for Indigo paste.

Preparation of the Dye-vat.

Dye-vat.

To render harmless the atmospheric oxygen dissolved in the water of the dye-vat a preliminary addition of hydrosulphite is made. For every 100 gallons of water add $^3/_4$—1 oz. Hydrosulphite conc. B. A. S. F. powder, stir well and allow to stand for some hours. Then introduce the whole or the requisite portion of the stock vat into the lower part of the dye-vat by means of a pipe widened above into a funnel, stir thoroughly and commence dyeing, provided, of course, that the vat is clear and yellow in colour.

The hydrosulphite vat is kept at a constant strength and in correct reduced condition by replenishing with stock vat and springing with hydrosulphite; these operations may take place during the working of the vat. The quantities of stock vat for replenishing are regulated as required, the average amount of hydrosulphite necessary is 2$^1/_2$ oz. per 100 gallons, or in the case of the continuous vat about $^3/_4$ pint of the solution prepared according to the directions on page 85 per 100 gallons.

In the continuous vat the additions are made to the bottom of the vat through the funnel-pipe mentioned, and they are distributed throughout the liquor by a stirring arrangement or by the movement of the goods through the vat.

---

* If it is preferred to work in a weakly alkaline vat, less than the above amount of caustic soda may be taken.

In working the vat great care must be taken that it contains neither too much nor too little hydrosulphite. The latter condition is recognised by the oxidation taking place too quickly, white material should be yellowish green and not green or bluish when it leaves the vat and should only slowly change through green into blue. On the other hand, if an excess of hydrosulphite is present the indigo goes too slowly on to the fibre or may be stripped off again. In this case the depth of shade does not correspond to the number of dips or to the concentration of the vat and dull, streaky dyeings result. The presence of an excess of hydrosulphite is shown by an intense golden yellow colour of the vat and by the fact that oxidation takes place too slowly.

With regard to the alkalinity it is necessary to remember that the vat must not contain too much caustic soda or the levelness and the shade will both suffer, nevertheless, there must be so much soda present even in weak vats (such, for instance, as are used in yarn dyeing) that the liquor has a smooth feel and turns phenol-phthalein paper distinctly red.

If a hydrosulphite vat remains for some time without being worked, it may happen that the indigo separates out in a compact form, and, owing to the great dilution of the vat, can only be brought into solution with hydrosulphite with difficulty or very slowly. In such cases the vat can be brought back into condition more rapidly by warming it by means of steam to about 100° F., thus assisting the action of the hydrosulphite.

When a hydrosulphite vat has been worked for a long time the salts which have accumulated in it may cause streaky dyeings in the case of piece-goods. It is, therefore, advisable to exhaust the vat when it shows a strength of over 15° Tw. or to pass a number of dry pieces through it and then replace with water the vat liquor thus removed.

Goods dyed in the hydrosulphite-soda vat need not be soured and are merely rinsed in water. The indigo removed in washing can be recovered according to the instructions on page 102.

The penetration of thick materials may be improved by warming the vats to 90—100° F.

d) The Bisulphite-zinc-soda Vat.

Bisulphite-zinc-soda Vat.

This vat is distinguished from the one last described by the fact that instead of ready prepared hydrosulphite a mixture of bisulphite and zinc dust is employed for the reduction of the indigo.

The vat has various disadvantages compared with the pure hydrosulphite vat. Firstly, it contains a sediment, since the amount of caustic soda does not suffice to dissolve the precipitate of zinc, secondly, a rapid accumulation of salts takes place in the vat, and this causes unlevel dyeing, lastly, the effective yield of the indigo is not so great as when ready prepared hydrosulphite is used. The longer the stock vat stands the more indigo is destroyed and its dyeing value lost, the cause of this loss is the zinc dust, which in all cases has a more or less injurious action upon indigo.

A series of experiments showed the following losses of indigo (estimated in the dye-vat itself):

1. After allowing the stock vat to stand for 2 hours, 5·6 %
2. » » » » » » » » 18 » 19 %
3. » » » » » » » » 36 » 22·15 %
4. » » » » » » » » 48 » 29·8 %

It is thus evident that the stock vat must not stand unnecessarily long, but whenever possible should be freshly prepared.

For the bisulphite-zinc-soda vat the same brands of Indigo pure are suitable as for the hydrosulphite-soda vat. The paste brands are used as supplied, the powder brands must be made into paste before use as directed on page 83, the pieces must be wet ground.

As with the hydrosulphite-soda vat, so here, a stock vat is first prepared, which is then used for setting and replenishing the dye-vat.

Stock Vat.

Preparation of the Stock Vat.

Make

100 lbs. Indigo pure 20 $^0/_0$ (or corresponding amounts of other brands) into a paste with about
4 gall. of cold water and
8 » bisulphite 57° Tw. Add to the mixture
8 lbs. zinc dust previously made into a paste with a little hot water, and stir the whole well for about $^1/_2$ hour. Let the mixture stand for another $^1/_2$ hour, and then add with constant stirring
12 gall. caustic soda 42° Tw. (or 6 gall. at 76° Tw.).

Make up the whole with hot water to about 60 gallons keeping the temperature of the mixture at 110—120° F. The stock vat is ready for adding to the dye-vat when it shows the right colour when tested with a strip of glass as described under the hydrosulphite-soda vat. Reduction is usually complete in half an hour.

Dye-vat.

Setting the Dye-vat.

For medium and concentrated vats it is advisable to add first for every 100 gallons of vat liquor a previously prepared mixture of $^1/_2$ pint bisulphite 57° Tw. and $^3/_4$ oz. zinc dust, to which after about $^1/_2$ hour's standing $^1/_8$ pint caustic soda 76° Tw. has been added. Then add the requisite quantity of stock vat, stir well, and commence dyeing as soon as the sediment has settled and the vat appears clear and greenish yellow.

When after working for some time the liquor has become greenish, and is no longer in a properly reduced condition, it is sprung with a mixture of

1—2 pints bisulphite 57° Tw. and
$1^1/_2$—$3^1/_4$ oz. zinc dust, to which after 15 minutes
$^1/_4$—$^1/_2$ pint caustic soda 42° Tw. has been added
} per 100 gall.

The mixture of bisulphite, zinc dust, and caustic soda is stirred carefully for 10—15 minutes and then added to the vat, which in a short time is again ready for use.

Stock vat is added as required together with a sufficient quantity of the reducing mixture (as given above). If the vat is too strongly reduced the hanks or pieces appear yellow; the proper colour is greenish yellow.

It is sometimes preferred to use lime instead of caustic soda, *i. e.,* to employ a

e) Bisulphite-zinc-lime Vat.

Bisulphite-zinc lime Vat.

Lime has the advantage that it does not attack the hands of the workmen in yarn dyeing, it produces, however, a larger sediment in the vat and renders a souring of the dyed material necessary. The disadvantage of the loss of indigo in the vat, especially when the stock vat stands too long, is met with in the lime vat just as in the soda vat.

In the recipe given above the caustic soda is replaced by 30 lbs. of quicklime previously slaked to a smooth, even paste, otherwise the preparation of the stock vat and dye-vat is the same as there given. For sharpening the vat $3\,^1/_4$ oz. quicklime previously slaked to a thin paste are added to the mixture of 2 pints bisulphite 57^0 Tw. and $3\,^1/_4$ oz. zinc dust.

f) The Hydrosulphite-ammonia Vat.

Hydrosulphite-ammonia Vat.

This vat is also without injurious action on the hands of the workmen; besides this both the hydrosulphite-soda vat and the hydrosulphite-ammonia vat possess the advantage of forming no sediment, and it will be found unnecessary to sour the dyed material; for this reason the hydrosulphite-ammonia vat is of interest for dyeing **cotton yarn** in hank and is especially to be preferred to the zinc-lime or the copperas vat, where great stress is laid on a vat without sediment.

In the following instructions we refer to an addition of common salt to the vat, the only object of this is to bring the dye more quickly on to the textile fibre, for it is possible thus to dye the same dark shade in half the number of dips which are necessary with other vat processes; and for this reason the hydrosulphite-ammonia vat is also suitable for dyeing loose cotton, already referred to on page 75. In this vat one can dye with advantage cotton yarn in hanks in large lots at a time; in this way a great economy in working results and a more rapid production than in other dyeing processes where the hanks are dyed singly.

One disadvantage with the hydrosulphite-ammonia vat is that in lighter shades it gives duller colours, and in darker shades less coppery tones than are obtained in the hydrosulphite-soda vat, and especially in the zinc-lime vat and the copperas vat.

Dyeing of Cotton Yarn in ordinary Dye-becks.

1. Dyeing of Cotton Yarn, large Lots at a time, in ordinary Dye-becks.

For 100 lbs. cotton yarn:

Dye liquor: 180—220 gallons,
Shade: Deep medium blue in 2 dips.

The cold dye liquor is previously "sprung" with

4 oz. Hydrosulphite conc. B.A.S.F. powder,
1/5 pint caustic soda 42° Tw.,

and an addition is also made of

1 gall. Turkey red oil F, Turkon oil or similar product,
9 lbs. common salt (previously dissolved in hot water).

One of the following stock vats prepared with *Indigo solution* or *Indigo pure powder L* is then added:

a) With Indigo solution:

24 lbs. Indigo solution B.A.S.F. 20 %,
7 gall. boiling water,
2 pints caustic soda 42° Tw.,
2 lbs. 10 oz. Hydrosulphite conc. B.A.S.F. powder,
2 pints ammonia S.G. 0,936 (about 17 %).

b) With Indigo pure B.A.S.F. powder L:

5 1/4 lbs. Indigo pure B.A.S.F. powder L,
9 gall. boiling water,
1 1/2 » caustic soda 42° Tw.,
5 1/4 oz. Hydrosulphite conc. B.A.S.F. powder,
2 pints ammonia S.G. 0,936 (about 17 %).

The mixtures are allowed to stand for about 1/2 hour until they possess the correct yellow colour. After the stock vat has been stirred into the dye-vat, dyeing can immediately be commenced. The yarn, previously well boiled out, is turned several times under the surface of the liquor on bent rods. After 20—30 minutes' working it is taken out, wrung out one hank at a time and oxidised. The dyeings are rinsed only, not soured. The liquor should be yellow to greenish yellow in appearance; if it is dark green or blue it must be sprung with $^1/_2$ lb. hydrosulphite and $^1/_2$ lb. caustic soda 42° Tw. per 200 gallons until the correct colour appears. The liquor should always smell slightly of ammonia. During regular work a daily addition of 1—2 pints ammonia will be sufficient. The vat is replenished with stock vat as required, $^1/_2$ lb. common salt (previously dissolved) being added per gallon Indigo solution. When the liquor shows 9° Tw. no more common salt is to be added.

2. *Dyeing of Cotton Yarn in single Hanks, Cops, Warps, and Pieces.*

The setting of the stock vat and the working of the dye-vat are carried out as described under 1. In the case of thin piece-goods the Turkey red oil may be omitted.

3. *Dyeing of Loose Cotton.*

To ensure the dry cotton becoming thoroughly wetted out in the vat, it is imperative to use Turkey red oil or some similar product. Stock vats and dye-vats are prepared as given in 1. Duration of dyeing process = $^1/_2$ hour. Cotton dyed in machines must be immediately hydro-extracted after dyeing; if dyed in an open vat, well squeezed out. The process is completed by a thorough rinsing.

g) The Fermentation Vats.

Fermentation Vat.

Vats of this kind for cotton, linen, etc., are only used on the small scale in Europe, but in tropical and oriental countries they are extensively employed by the natives. Their use is traditional, and they will probably continue to be used in these countries, as they are so well suited to the conditions there prevailing, *viz.,* cheap labour without industrial pressure or demand for rapid production.

During the process of fermentation, products are formed which impart to the dyed material a peculiar odour, the so-called "indigo smell." The dyeings are also deeper and less coppery in shade than in the case of the other cotton vats. Both these properties are demanded by the consumers in many districts, and this fact increases the probability that the use of fermentation vats will be continued. Material dyed in the fermentation vat is also rather heavier than when dyed in chemical (zinc-lime or hydrosulphite) vats.

Since this method of dyeing plays hardly any part in connection with European industry, we shall only describe it in general terms.

The reduction of the indigo is brought about by the evolution of hydrogen gas due to fermentation, and this fermentation depends upon a bacteriological action upon the fermentative substances containing sugar or starch, which are added to the vat. This process of decomposition or fermentation takes place in the presence of an alkali.

The ferments employed are of very diverse nature and are chosen according to local conditions, the following substances amongst others are used: bran, flour, syrup (molasses), bread, dates and other sugar-containing fruits, wine, henna leaves. The alkalies used are lime, potash or wood ashes, soda, caustic lye prepared from wood ashes and lime, also naturally occurring soda (known as "illig" or "kallia" in Syria, Persia, and Thessaly, "kischmisch" in Central Asia, "kalagar" in the Caucasus), and occasionally urine. The functions of the alkali are to regulate the course of the fermentation process, and at the same time to dissolve the indigo white which is formed from the indigo by this process. A certain excess of alkali retards the fermentation and may even arrest it altogether; should too little alkali be present, a decomposition of the fermenting substance takes place or the fermentation which causes evolution of hydrogen becomes so violent that the indigo is thereby partially or wholly destroyed. The addition of alkali to the vat is called "sharpening." If the vat contains too much alkali it is "over-sharpened," if too little it is "mild" or "sweet."

The vats are set and worked according to long-known empirical rules; exact recipes and directions for the working of fermentation vats cannot be given. Each vat, so to speak, must be treated individually, since, even when vats are set in the same way, variations occur in the course of the fermentation process. The dyer must be able to judge day by day in each separate case on the basis of his own practical experience what additions must be made and in what quantities.

The appearance, smell, and taste of the vat, the behaviour of the flurry, and the vigour of the fermentation are the points to be noted by the dyer. Phenol-phthalein paper, which is turned more or less strongly red by the vat liquor according to the alkalinity is very useful for ascertaining whether the vat is sufficiently or too strongly alkaline.

Brands of Indigo for the Fermentation Vat.

The following brands are suitable for use in the fermentation vat:

Indigo pure B. A. S. F. paste 20 % S,
» » » powder SL,
» » » powder S,
» » » pieces S,
» » » paste 20 % E,

and in addition to these the special brands

Indigo pure B. A. S. F. powder 40 % E,
» » » powder 60 % E,
» » » grains 40 %,
» » » grains 60 %.

The *G* and *R* brands may also be used, the latter being more suitable for the cold than for the warm vat. It is necessary to decide in each individual case which of these brands should be selected. The *S* brands are chiefly to be preferred for those vats which are worked warm with the addition of fermenting agents, *e. g.*, the potash vats, whilst the *E* brands are specially suited for the cold vats which contain little or no fermenting agent.

Indigo Vat and Indigo White.

The brands

Indigo Vat B. A. S. F. 60 %,
Indigo White B. A. S. F. E extra and
Indigo White B. A. S. F. E double

offer exceptional advantages for fermentation vats. They contain the indigo in a ready reduced condition and dissolve directly in the vat, thus offering the advantage of a rapid, productive, and at the same time safe method of working. In the same way can be applied

Indigo solution 20 %.

Indigo solution B. A. S. F. 20 %,

which also dissolves immediately in the vat without waiting for the fermentation process, and it may, therefore, serve in case of need to increase the productive capacity of the vat.

With regard to the method of application of the various brands the following points should be noted: the paste brands, Indigo solution 20 %, and Indigo vat 60 % are added directly to the vat; powder SL is previously made into a paste (see page 82); powder S, also powder E, and the grains are rubbed into a paste with vat liquor or water; Indigo White B.A.S.F. E extra is previously dissolved with lime and vat liquor.

Description of the Vats.

The vessels are usually smaller than the fermentation vats used in wool dyeing. The vats which are worked warm, such as the potash and bran vats, contain on the average 45 gallons, the cold vats used in the East only about 20—30 gallons; these latter are made of clay and are sunk in the ground. The Chinese also employ larger, cemented vats, which may even contain several hundred gallons. In Japan, however, small vats of about 45 gallons are used. These are clay vessels narrowing to a point below, several being heated by a single fire of charcoal, sawdust, etc.

It would occupy too much space to describe all the various methods of setting fermentation vats for cotton, linen, etc., so that we confine ourselves here to a few typical examples.

One of the most largely employed of the warm vats is the

Potash Vat.

Potash Vat.

The vessel used is generally a copper vat tapering to a point below, partially walled in, and heated either by direct fire or by steam.

The following proportions have been found to serve well for setting a vat of about 40 gallons:

3 lbs. madder,
3 » potash,
2 » Indigo pure 20 % S (or a corresponding amount of some other brand),
3 » bran.

These substances are added to the water in the vat, which has been heated to 130—140° F.; the bran should be added last of all, being strewn on the surface of the vat after the latter has been well stirred, and allowed to sink by itself. The vat is now covered and allowed to stand quietly at a temperature of 120—130° F. On the second day, when fermentation begins and the red colour of the madder disappears, it is sharpened with potash, adding about 1 lb. at a time. On the same day the vat is strengthened by the addition of 2 lbs. Indigo 20 °/o S, and this is repeated on the third day. The vat is worked exclusively with potash, of which such quantities are added that phenol-phthalein paper is always coloured distinctly red.

The vat is ready for dyeing when the liquor is clear and dark yellow, the sediment is yellow, and a considerable flurry has formed.

When the vat is exhausted it is replenished with indigo and bran or madder, and, if the vat is in good condition, the indigo will be dissolved in about 12 hours. Dyeing takes place at about 120° F., after dyeing the material is not rinsed but at once dried.

The potash vat is worked in Russia with rye flour or bread as fermentative agent.

Bran Vat.

Bran Vat.

This vat is employed in Italy and possesses the advantage of being free from sediment, it is, therefore, capable of being worked for a longer time. Old vat liquor is always used for setting the vat, since it takes too long to start the fermentation in fresh water. For a vat containing 100 gallons may be used

18	lbs.	Indigo 20 °/o S (or preferably the corresponding amount of E brands or grains),
6	»	potash, and the decoction from
30	»	bran.

The bran is boiled up with about 20 gallons of water, and the decoction poured through a sieve into the vat containing the old liquor. The vat is set at 120° F. and maintained at this temperature. On the day after setting the liquor is green and is sharpened with caustic potash at about 15° Tw., generally prepared by the dyer himself from wood ashes and lime. Occasionally carbonate of potash is used for sharpening the vat.

The colour of the liquor changes in the course of 3—4 days to a dark yellow, and the vat is then ready for dyeing. It is kept sufficiently alkaline to redden phenol-phthalein paper distinctly. To assist the action of the bran decoction an addition of flour is sometimes made.

Cold Fermentation Vat.

The

Cold Fermentation Vats

are never started with fresh water, but always with liquor and sediment from old vats. The exhausted vat is replenished with indigo; where no fermenting agents are added, the *E* brands or Indigo vat 60 % must be used and the vat worked by means of lime alone or natural soda and lime. In the hot season the indigo is dissolved in about 3 days, but in winter this takes 5—6 days or longer. The fermentation is sometimes assisted by additions of syrup (Egypt, Syria) or dates (Bagdad, Persia). In China the lees from the manufacture of rice spirit (samshu) or the spirit itself is used as ferment.

Cold vats, when in good condition, have a pure yellow liquor and sediment, they have a strong permanent flurry, and impart a distinct red colour to phenol-phthalein paper.

If the sediment accumulates too much when the vat has been worked for a long time, a portion of it is removed from the vat.

In Japan the vats are set warm but used for dyeing at the ordinary temperature. The method of setting and working is subject to many variations, as a rule the impure Japanese indigo, which only contains a small percentage of colouring matter, is used as a ferment in the same way as we employ woad, frequently bran is also used; the vat is sharpened with wood ashes and powdered lime.

13. Calculation of the Cost of an Indigo Dyeing on Cotton, Linen, etc.

Calculation of the Cost of an Indigo Dyeing on Cotton, etc.

The question often arises as to the cost of a particular shade of indigo on yarn or piece-goods. An answer that would be correct in every case cannot be given to such a question, but only a conditional one, which assumes that certain conditions are adhered to. In the preceding sections it has been repeatedly pointed out that the whole nature of the dyeing process influences the result to a great extent, also the details of the method of working play an important part in the calculation.

The amount of indigo used up in dyeing is the sum of:

1. the indigo fixed on the fibre,
2. the indigo destroyed in the vat, and
3. the indigo removed in washing and souring which is lost or is not recovered.

The amount of indigo fixed on the fibre is determined by means of extraction with glacial acetic acid. Estimations of the indigo on the fibre by comparison with dyeings containing known amounts of indigo are untrustworthy, since the quality of the yarn and the degree of penetration influence the result. The loss in the vat, which naturally varies very considerably, can on the average be taken as follows:

1. for the copperas vat . .	25 %	of the amount of indigo fixed on the fibre.
2. for the zinc-lime vat . .	10 %	
3. for the pure hydrosulphite-soda vat	2 %	

The mixture of bisulphite, zinc dust, and caustic soda sometimes employed may show a loss of 20—30 % if the stock vat has been allowed to stand for some time.

The amount of indigo removed from the yarn in washing varies, as already mentioned, from 4 to 12 %, and in piece dyeing from 12 to 25 %, so that for each shade an average percentage must be reckoned, *e. g.,* for the usual dark blue on yarn 10 %, for medium and dark blues on pieces 20 %. If the indigo is recovered the loss may be reckoned as one-quarter to one-third of the above, *i. e.,* at about 3 % for yarn or 5—6 % for piece-goods.

The cost of reducing agents and alkali besides labour and general expenses, which vary from one case to another, must be added to the cost of dyestuff.

From these data the cost of dyeing can approximately be calculated, but we would emphatically point out that, as can readily be gathered from the foregoing statements, the several items of the calculation are not constant, but according to the circumstances are subject to important fluctuations, so that the cost of production of the same shade will vary to a considerable degree.

14. Recovery of the Indigo removed in Washing and Souring.

Recovery of the Indigo removed in Washing and Souring.

The recovery of the indigo removed in washing and souring is strongly to be recommended in all dyehouses where indigo dyeing is regularly carried on.*

The first souring and rinsing baths, which contain a considerable amount of dyestuff, are used for the recovery of indigo. The working up of the vat sediment to recover indigo necessitates a special and somewhat complicated treatment and is without practical interest, since the yield does not justify the expense.

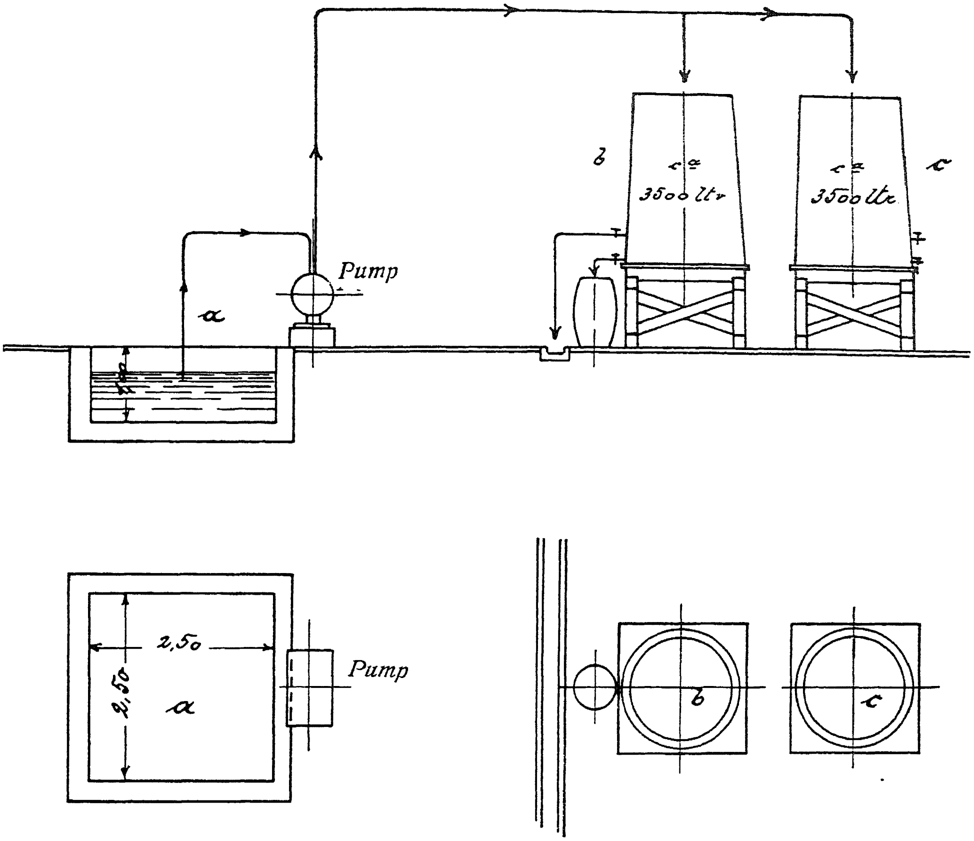
The nature of the plant used for the recovery of the indigo naturally depends on the local conditions, differing according to the amount of effluent to be treated, the space at disposal, the nature of the ground, and the tanks, cisterns, and reservoirs at hand. We give below a description of a few varieties of plant; these are merely described in general principle and can be altered within wide limits according to circumstances.

The simplest form of plant consists of two water-tight (*e. g.*, cement) pits or cisterns in the ground, in which the effluent is caught; in small dyehouses tubs may suffice. They are used alternately; when one is full it is allowed to stand for a day or two until the indigo has settled to the bottom. The clear water standing above it is pumped away, and the blue, slimy sediment is shovelled out. During this time the effluent is being collected in the other pit or cask.

Figs. 7 and 8 show a plant of another kind. The effluent is collected in a water-tight cistern *a,* let into the floor of the dyehouse, and pumped from there as required into two reservoirs *b* and *c,* erected about 4 feet above the ground at a suitable spot outside the building. When one reservoir is full, the liquid in it is allowed to stand for some time in order that the indigo may settle, and meanwhile the other reservoir is used. Each reservoir is provided with two taps, one at the bottom, the other 10—12 inches higher. To empty the reservoir, the clear water is first drawn off by means of the upper tap, and the sediment of indigo is then run into a suitable vessel by means of the

---

* *Dr. Fürth,* Lehne's Färberzeitung, 1900, p. 204.



Figs. 7 and 8. Plant for the Recovery of the Indigo.

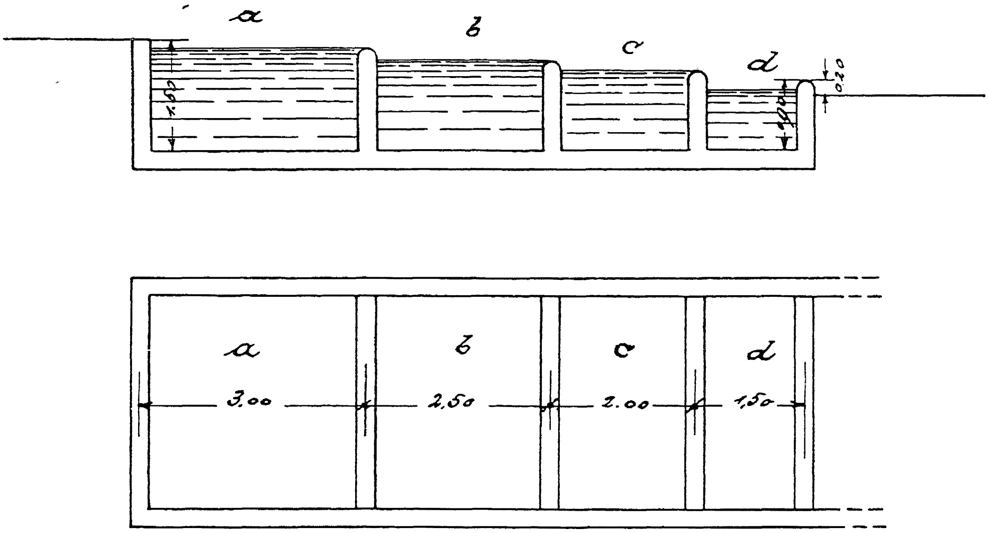


Fig. 9. Cascade System for the Recovery of the Indigo.

lower tap. The reservoirs may be of wood or iron, in the latter case an old vessel of any shape whatever will serve the purpose. If the effluents containing indigo are acid they must be neutralised with lime in the collecting cistern.

Fig. 9 illustrates the cascade system. This may be built into the floor of the dyehouse itself or erected outside; it requires the ground to be sloping, so that the effluent can run out of the last compartment. The arrangement can readily be seen from the sketch, of course all measurements can be altered as may be necessary. There should be at least three compartments. The effluent is collected in the first compartment *a,* and most of the indigo settles out here, the water running over carries a part of the dyestuff with it to the second compartment *b,* where a further portion of the indigo is precipitated, and so on in the following compartments. When *a* is to be emptied, the effluent is allowed to run for a few days into *b,* and during this time *a* is not disturbed. The clear water is then pumped out of *a,* and the sediment of indigo is dug out. Very little indigo collects in the third and fourth chambers, so that they need only be emptied at long intervals when opportunity occurs. The compartment *b* must be emptied when *a* is being filled. The effluent may run into the cisterns, when these are fixed in the ground, either by means of a sloping floor or by suitable gutters or pipes.

It is very advisable to have a filter-press for the indigo sediment. In this way the recovered indigo is obtained in solid cakes instead of in the form of a thin paste, which retains many impurities soluble in water (mineral salts, etc.). In the arrangement shown in Fig. 7 the filter-press is erected near the reservoirs *b* and *c* in the place of the cask shown in the figure, in other cases near the cistern. In all cases the thin indigo paste is pumped into the press through a suction pipe by means of a simple suction and pressure pump fitted to the press.

The employment of the indigo as obtained, *i. e.,* the mixture of water and indigo, for setting new vats, as is sometimes done, is unhesitatingly to be condemned. This would cause a rapid accumulation of soluble salts in the vat, the bad effect of which would be apparent in the resulting dyeings.

The recovered indigo is not pure, it contains as impurities the waste matters removed from the material in washing and souring, such as fibres, size, etc. The lower the quality of material dyed the less pure will be the recovered indigo, and it will contain more impurities, for example, when washed from unbleached linen than from ordinary cotton. Reckoned as dry substance it should contain 45—65 % indigo. The exact amount of indigo removed from the fibre and recovered cannot be definitely stated, the figures vary within wide limits according to the material, the shade, and the method of dyeing from 4 up to 40 % and more (see page 101).

It is not to be recommended to use the recovered indigo alone either in the pressed condition or as a thin paste, but it may be mixed in a definite proportion with fresh indigo when setting a new vat. The proportion of pure indigo may be calculated most simply once for all as follows: Any definite quantity, say 2—4 lbs. or less, is quickly dried in a suitable vessel, and half the dry weight is reckoned as pure indigo.

Example:

4 lbs. pressed cake gave on rapid drying
20 oz. of residue. The half of this =
10 » pure indigo in 4 lbs., or
$2^1/_2$ » in 1 lb. of pressed cake.

Or:

4 lbs. of sediment gave
6 oz. of residue, corresponding to
3 » of pure indigo in 4 lbs.,
$^3/_4$ » in 1 lb. of sediment.

It will often simplify the calculation to reckon 1 gallon of sediment as equal to 10 lbs. The resulting figures are only approximate, but permit of a fairly close calculation.

Occasionally the whole of the recovered indigo is used in a special vat for tinting or some other definite purpose, or a stock vat is prepared from it, and this is divided among the vats in work.

All these methods of application and the process of recovery itself can, of course, be varied to suit the local conditions according to the object and desire of the dyer.

15. Linen, Linen and Cotton Unions, and Jute.

Linen. Jute.

The methods of working in dyeing these materials are the same as for cotton. Piece-goods are dyed almost exclusively in the dipping vat worked according to the zinc-lime or copperas methods, the continuous vat is not employed. To obtain good penetration for plain coloured linen materials, long dips (6-10 hours) must be given commencing in an exhausted vat. For resist prints the dips must last only 5—15 minutes or the resists will be dissolved away.

Linen yarn and jute yarn (the latter is very seldom dyed with indigo) may be dyed in any of the vats used for cotton yarn and are treated in exactly the same manner.

Part II.

The Application

of

Indigo pure B. A. S. F.

in

Calico Printing.

INTRODUCTION.

The Chemical Basis of Indigo Printing.

It can hardly be doubted that the art of applying indigo not to the whole of a fabric, but merely to certain portions of it, thus producing a more or less regular pattern, is as old as its employment in dyeing.

Methods for fixing Indigo on the Fibre:
a) by Reduction into Indigo White and Re-oxidation.

Indigo, as is well known, can only be fixed on the fibre in dyeing by being first converted by a reducing agent into indigo white, the latter being at the same time dissolved in alkalies. From the solution of indigo white thus obtained and known as a "vat," both animal and vegetable fibres are able to take up a portion of the reduced colouring matter, which when exposed to air is changed by the atmospheric oxygen into indigo blue, and this is deposited in the fibre. The same properties of indigo are made use of in almost every case for fixing the dyestuff on the fabric in calico printing. There are, however, one or two processes carried out industrially to a limited extent, which depend not on the formation of a vat, but partly on the ease with which indigo sublimes, partly on the direct production of indigo on the fibre.* These processes, which do not depend on the application of the reduction product, have all been introduced during the last decade, and those of the second class named may be regarded as precursors of the synthetic production of indigo, the introduction of which has caused the opening up of new avenues of development in the printing of fabrics with indigo.

b) by Sublimation.

c) by Production of the Dyestuff on the Fibre.

---

* The further possibility of precipitating indigo from solutions containing it as such in an insoluble form on the fibre by a single operation does not seem capable of technical application. A proposal of this kind for the use of colloidal indigo is mentioned in the Zeitschrift für angew. Chemie, 1903, page 47.

Methods for the Production of Patterns.
a) by Resist Printing.

The simplest method for the production of patterns consists in protecting certain portions of the fabric in some way before dyeing (resist process).

There are two properties of indigo, which are of great value in all such resist processes on fabrics of vegetable origin — and we have to do with these fabrics in practice almost exclusively — *viz.,* its power of being fixed firmly and permanently firstly at the ordinary temperature and secondly in a very short time, since by prolonging the dyeing operation or by raising the temperature, there is always a danger of dissolving the resisting substances from the fabric. On account of these useful properties the methods of resist printing have possessed an importance from the very beginning up to the present day in connection with indigo, which is not even approximately approached in the case of any other dyestuff.

b) by Direct Printing.

The second method of producing patterns on fabrics consists in applying the dyestuff in solution to portions of the fabric only; to prevent the solutions from running they must be suitably thickened. The above-mentioned properties of indigo of becoming fixed on the fibre almost instantaneously and at the ordinary temperature are of great assistance, but, on the other hand, the sensitiveness to air of the thickened vat solutions is the cause of various difficulties.

Although a satisfactory reply to the demand for a good printing process for indigo was first made less than a generation ago, and the question of a perfect method, which allows of indigo being printed at will along with other colours, still awaits solution, yet the most primitive methods of this kind are very old indeed. We have been brought nearer to the goal of the unrestricted application of indigo along with other colours in calico printing through the recent introduction of formaldehyde-sulphoxylate (Rongalite C) as a reducing agent, and the hope of a completely satisfactory solution of this problem need not be abandoned in spite of all the difficulties due to the peculiar nature of indigo.

c) by Discharge Printing.

The third principle of forming designs, *viz.,* discharge printing, which depends upon the partial destruction of the colouring matter on the evenly dyed fabric, was the last to find application in the case of indigo. Since the methods of discharging involve a thorough chemical knowledge, this order of development in the processes of indigo printing is not surprising. Indigo is also, as it were, suited by nature for discharge printing, since in spite of its great resistance to most agencies it is readily converted by oxidising agents into isatin, which no longer possesses the character of a colouring matter and is comparatively easily soluble. The methods of discharging indigo are, therefore, simple and reliable, and the production of coloured discharges also offers no difficulty. The whole development of discharge printing on an indigo ground from its commencement to the present stage has occurred during the last century, and we can, therefore, trace with exactitude all the phases of this development.

d) by Combination of the three Methods.

The three general methods of producing patterns based on the principles described above, *viz.*, resist printing, direct printing, and discharge printing, are not only employed separately for indigo, but many processes are in use which depend upon a combination of two or indeed all three of these methods.

1. Resists.

For example, effects, which will be described later on, are exclusively produced on the practical scale by the use of resists, which on the one hand exercise a discharging effect on the dyed indigo ground and on the other hand protect the printed portions against a further dyeing process. It is also a common method to first print the material, then dye over this, and on the mixed pale blue and dark blue ground thus obtained to print white or coloured discharge patterns. Lastly a resist may be applied which prevents the fixation of indigo afterwards printed over it.

2. Direct Printing, Dyeing-over, and Discharge Printing.
3. Resists under Direct Printing.

Although the simpler methods of forming patterns are common to indigo and other dyestuffs (modified, however, in the case of indigo to suit its special properties), most of the processes depending on the combination of two methods as just described, are peculiar to indigo alone.

Our description would not be complete did we not mention two further methods of forming designs, which, although not so widely used as those already referred to, still find considerable application in indigo printing.

e) by Printing with Substances which produce in the Dyeing-over darker Shades on the printed Parts.

The first of these and thus the fourth method in our series, is the reverse of the resist process, inasmuch as a substance is applied to certain portions of the fabric not to prevent but to further the deposition of colouring matter, so that a dark pattern on a paler ground of the same tone results. In the case of indigo the same effect is produced in this way, in a simpler and, it may be here remarked, less perfect manner, than results from direct printing in combination with previous or subsequent dyeing in the vat.

f) by Printing with Covering Pigments.

The fifth method consists in printing on the dyed ground together with some adhesive substance coloured pigments, which completely cover the ground in the printed portions. Oil and bronze colours are used in this way. This method of decorating woven materials is really the oldest of all, and in spite of all the disadvantages involved and all advances in the technique of calico printing it is still employed, at any rate in small works, and also to a certain extent in combination with the resist process.

Classification of the Processes used in Indigo Printing.

Classification of the Processes used in Indigo Printing.

On the basis of the principles detailed in the foregoing section, by making use of which designs may be produced in calico printing with the aid of indigo, the processes employed in indigo printing may be divided into five groups of varying extent and importance. According to the mechanical or chemical substances used in various cases they may be further arranged in subdivisions. In the following survey we abandon the order of description in the introduction and select one which permits of the clearest and simplest description possible of each single process and the relations of the various processes to one another. From this point of view the classification is as follows:

I. **Printing of covering pigments on previously dyed goods.**
   1. Printing of bronze colours with albumen;
   2. Printing of oil colours.

II. **Printing of substances on the undyed fabric, which increase the depth of shade of the printed portions on dyeing in the vat.**
   1. Printing with oxidising substances (metallic salts and sulphur);
   2. Printing with substances having a mercerising action.

III. **Fixing the colouring matter by sublimation** (*Dr. Elbers'* process).

IV. **Direct printing with indigo.**

1. Printing of indigo in a reduced state:
   - a) Brushed or painted blue,
   - b) Solid blue,
   - c) Printing with hydrosulphite, etc.
2. Printing of indigo with subsequent reduction on the fibre:
   - a) Fayence blue printing. Printing indigo with subsequent reduction in the copperas vat;
   - b) *Schlieper's* process and variations of it, reduction by means of dextrine, glucose, or maltose in the steaming operation;
   - c) Rongalite process. Reduction with formaldehyde-sulphoxylate.

V. **Production of indigo on the fibre*** (from indoxyl, *o*-nitrophenyl-lactic acid-ketone, formaldehyde-indigo white, etc.).

VI. **Discharge printing on indigo.**

1. Destruction of the dyestuff by reduction, stannous chloride discharge;
2. Destruction of the dyestuff by oxidation:
   - a) Chromate discharge,
   - b) Chlorate and bromate discharge.

VII. **Resist printing under indigo.**

1. Purely mechanical resists:
   - a) By tying,
   - b) Battik printing, wax resist,
   - c) Japanese stencil method,

   } chiefly in use in Eastern Asia.
2. Chemically and mechanically acting resists with acid and oxidising salts together with indifferent substances (the blue print process in the narrow sense).

---

* This process is mentioned here only for the sake of completeness, and we will not describe it in detail, since it now possesses only historical or theoretical interest and has also been partially supplanted by the new simple printing process with Rongalite C.

Combined Printing Processes.

The above methods may be combined with one another to an almost unlimited extent, so that the number of possible processes and indeed of those still partly in use is considerably greater.

Since the designs produced can be coloured in various ways, and also applied along with other colouring matters, indigo printing includes the production of an incalculable multiplicity of effects, such as is not even approximately attained by any other colouring matter, and this lends a special charm to the study of this branch of printing. It will be understood that only those processes which are of general importance can be fully dealt with in the following pages.

In the case of obsolete methods or such as are only of local importance, reference is made in a foot-note to the first or best description of the process in other works.

I.

Printing of Covering Pigments.

Bronze and Oil Colour Prints.

Printing with Covering Pigments on Indigo dyed Fabrics.

The most widely used process for the printing of covering pigments, *viz.,* printing with mineral colours or colour lakes which are fixed with albumen, is not made use of by itself on indigo dyed fabrics, because the indigo can be destroyed at the same time on the printed portions by suitable means in a simple manner, thus obtaining much more complete effects.

Two other processes for the decoration of indigo dyed material are used, however, in which pigments are printed on the fabric without simultaneously discharging the ground, *viz.,* printing with finely divided metallic bronze colours, and printing with ordinary oil colours.

Bronze Prints.

The decoration of dyed materials by printing with metallic powders is carried out chiefly for the export trade; for pale shades gold bronze is generally selected, for dark shades silver bronze. As fixing agents have been proposed resin, india-rubber solution, varnishes, albumen, casein, etc.;* at the present day varnishes are employed either alone or better mixed with albumen. In the former case the colour is fixed by simply hanging up the material for a lengthened period, but when albumen has been used a steaming operation is also necessary. To bring out the characteristic metallic lustre of the bronzes the material must finally be calandered hot with strong pressure or rubbed with an agate. Pattern No. 1 shows the effect thus produced.

---

* See *Schützenberger,* Traité des matières colorantes, Paris 1867, vol. I, page 215, and *Lauber,* Praktisches Handbuch des Zeugdrucks, Leipzig 1901, vol. I, page 173.

Pattern No. 1.

Bronze print on indigo ground.

Oil Colour Prints.

The method of printing with ordinary oil colours is the most primitive and crude of all printing processes, it is probably never carried out except on an indigo ground. In certain districts of Germany it is still in use in small country dyehouses where garments, chiefly those already worn, are re-dyed in the vat and then printed with a pattern in oil colour, thus hiding irregularities and covering damaged portions of the fabric. Printing with oil colours has, however, found a further and much more extensive sphere of application in the Russian home industry. Since the method of producing patterns most suitable for these primitive conditions, *viz.,* resist printing, does not permit of the production of a brilliant red, the difficulty is overcome by printing a red oil colour on the white design previously obtained by the resist method. A mixture of vermilion and chalk is the red pigment chiefly used, this is rubbed together with linseed oil varnish and made up to a suitable consistency for printing. It is fixed merely by slow drying.

Pattern No. 2.

Oil colour print on linen.

As produced by Russian peasants.

As might be expected from the nature of the pigment colours, both the bronze print and the oil colour print are very fast to light, but in respect to fastness to washing they only satisfy the most moderate requirements.

We are not aware that materials other than cotton and linen are printed in this way. It will be evident from the foregoing description, that the method only applies to block printing.

II.

Printing of Substances on the Undyed Fabric which increase the Depth of Shade of the Printed Portions on dyeing in the Vat.

Production of Patterns by Printing with Substances, which increase the Depth of Shade of the Printed Portions on dyeing.

a) by Mercerisation.

It is well known that cellulose under the influence of strong alkalies or other substances exercising a similar action, undergoes a chemical alteration, which imparts to it the property of taking up most colouring matters in increased amount and fixing them more firmly.* Indigo is no exception in this respect; the mercerised cotton fibre (*i. e.,* cotton treated with strong caustic soda) is dyed in the vat considerably darker and faster shades than ordinary cotton under the same conditions. This property may be made use of for the direct production of dark patterns on a pale blue ground by printing slightly thickened caustic soda at 55—75° Tw. on the material and after washing dyeing in the vat. Pattern No. 3 has been produced in this manner

Pattern No. 3.

Design produced by partial mercerisation.

---

* Compare German patent No. 107916 of *Giovanni Tagliani.*

In some printworks, where for some reason or other the ordinary method of producing this effect, *viz.,* direct printing of indigo and subsequent dyeing, cannot be made use of, this process depending on partial mercerisation is being employed to obtain a patterned ground for discharge printing. The reason why it is not in general use for this purpose in spite of its cheapness and simplicity is that the difference in depth of shade between the pattern and ground is influenced by the varying condition of the vat (alkalinity, excess of reducing agents) in the course of working, and the results are, therefore, rather uncertain.

b) by Precipitating.

There is a further possibility, peculiar to indigo, of increasing the depth of shade by the application of such substances as are capable of throwing the dyestuff out of the alkaline indigo white solution either as indigo itself or in the reduced condition. Such substances are acids, acid or oxidising salts, and other oxidising agents. If compounds of this kind are fixed on the fibre, the depth of the shade is increased when it is afterwards dyed. An indispensable condition is that the precipitating substance is present in a state of great dilution, for otherwise it will prematurely exercise its precipitating action and act like a resist. The possibilities of producing designs in this way are, therefore, manifold, since the number of substances possessing the above property is great, but only a very few find practical application. First of all the acids are useless, or at least up to the present no suitable method for using them has been suggested. Of the oxidising agents manganese and copper salts, and more especially sulphur are of interest, and these substances in contradistinction to the alkalies, which attack the animal fibres, admit of the possibility of the application of the process to wool and silk. A process of this kind, depending on the use of manganese brown, is described and illustrated by *Persoz** in his book. We have more recently** proposed the use of sulphur, with which good results are obtained, especially on wool.

None of these processes have yet attained any great practical importance.

---

* *Persoz,* Traité de l'Impression, vol. III, page 44.

** Letters patent No. 23338 (1900).

III.

The Fixation of Indigo by Sublimation.

Indigo Grey according to *Elbers*' Process.

Fixation of Indigo by Sublimation.
Elbers' Indigo Grey.

In the course of an attempt to work out a process, which would permit of printing indigo along with any other dyestuffs, *Dr. Elbers* of Hagen discovered in 1898 a method,* which rendered it possible to produce both on animal and vegetable fibres, not certainly a blue, but a bluish grey very fast to light and fast enough to washing for most purposes. The process consists in printing finely divided indigo together with vegetable or animal oils, and then steaming the goods, preferably under pressure for some time. A repetition of the steaming increases the fastness to rubbing and soaping. The grey thus obtained behaves exactly like indigo dyed in the vat, and can be similarly employed for the production of discharge styles. The printing colours may also be mixed with Alizarine and Aniline colours, and in this way a great variety of shades fast to light, especially "mode shades," can be obtained. The fixation of the colouring matter here evidently depends upon the sublimation of the indigo from the printing colour attached to the threads on to the fibre itself.

---

* Letters patent No. 509 (1898) and No. 6546 (1898).

Printing Process
for
the Production of Fast Greys on Cotton with Indigo pure B.A.S.F. 20 %.

Indigo Grey on Cotton.

The material prepared for printing in the usual manner is printed or padded with a colour composed of

20—50 parts Indigo pure B.A.S.F. 20 %,
20—50 » olive oil,
960—900 » thickening (starch or flour paste),

and dried, then steamed for 1½—2 hours in a continuous steamer, or preferably 1½ hours in a closed (cottage) steamer at 12—15 lbs. pressure, washed, and soaped as usual.

Pattern No. 4.

Indigo grey on cotton.

If particularly good fastness to washing is required, the goods after washing (de-gumming) are re-steamed for 1—2 hours, preferably at 12—15 lbs. pressure; in this way the grey is fixed in a form more resistant to washing.

The printing paste for indigo grey may be added to any other tannin or mordant (chrome, alumina, etc.) printing colour; the grey can, therefore, be employed in combination with any of these colours.

The grey obtained according to the above process can also be discharged white or in colours according to the methods in use (*e. g.,* chromic acid discharge) for indigo blue (dyed or printed).

# Printing Process
for
the Production of Fast Greys on Wool and Silk with Indigo pure B. A. S. F. 20 %.

Indigo Grey on Wool and Silk.

The material prepared in the usual way is printed with a colour composed of

20— 50	parts	Indigo pure B. A. S. F. 20 %,
10— 20	»	olive oil,
970—930	»	thickening (starch or flour paste),

dried, steamed one hour without pressure, and finished in the usual manner.

The printing colour for Indigo grey may on account of its indifferent character be used for compound shades in combination with all other dyestuffs used in wool printing.

Direct Printing with Indigo.

1. Development of the Process.

Direct Printing with Indigo.
Development of the Process.

When indigo was first imported into Europe, the methods by which it was applied in the East Indies were also introduced into the same countries, which were at first England and Holland. The oldest process for the production of topical dyeings, *i. e.*, dyeings confined to certain portions of the fabric, all consist in conveying indigo white on to the material either in alkaline solution or in the free state with a subsequent passage through alkali. The various processes do not greatly differ from one another in principle, apart from the mechanical means by which the colour is applied, but only in the nature of the alkali (in the earlier days only lime and caustic potash were known, caustic soda came into use later), and more particularly in the nature of the reducing agent. At some time or other every reducing agent technically possible has been proposed and tried for the purpose of indigo printing so far as it permits of the preparation of sufficiently concentrated and stable vats.

At the period when indigo was introduced into Europe, orpiment vats prepared from trisulphide of arsenic, lime, and indigo were employed in India. In printing calico the pattern was painted on the material with the thickened orpiment vat by means of a little stick flattened at one end (the corrosive nature of the vat forbidding the use of any substance other than wood) or printed on with wooden hand blocks. When the printer learnt to replace the poisonous orpiment partly or wholly by ferrous sulphate, no change was made in the method of working. In both cases the colour was developed by hanging the goods in running water. This is the so-called brushed or painted blue now obsolete in Europe, but still employed to-day exactly in its original form in India in the home industry and by native printers. The discovery in England in the first quarter of the 19th century of the solid blue process* marks an important advance. In this process the indigo was printed in a reduced but undissolved state as indigo white, and brought into solution by a subsequent passage through alkali. To give the printing colour sufficient resistance to the action of the air, a reducing agent (stannous oxide) was added. This process, which caused in its day a revolution in indigo printing, is now obsolete.

Brushed or Painted Blue.

Solid Blue.

From various sources a number of printing processes based on similar principles have been suggested, but we cannot enumerate them all in these pages. The most worthy of notice is that of the discoverers of hydrosulphite, *Schützenberger* and *Lalande,* and is based on reduction with this product,** but this method, even when anhydrous Hydrosulphite B. A. S. F. is employed, has not been able to hold its own in the face of advances in other directions. The proposals of *Bancroft,**** to bring about the reduction by means of glucose, and of *Prud'homme,* who reduces with glycerine and caustic soda by the aid of a steaming process, also deserve mention. These proposals, in the form in which they were made, have no practical importance, but in them is to be found the germ of further development. From the combination of the use of glucose with a steaming process sprang *Schlieper's* process, which is still in use at the present time.

Printing with Hydrosulphite.

All the processes mentioned hitherto depend on the printing of free indigo white or an alkali salt of indigo white, and in addition to the inconvenience due to the sensitiveness of the colour to air they possess the great disadvantage that only a small part of the colour is fixed, so that, apart from the fact that the indigo is only partially utilised, it is hardly possible to produce blues of even medium depth from very concentrated vats. The reason of this behaviour cannot be completely understood with our present imperfect knowledge concerning the nature of the fibre and of indigo white. We have to be content at present with the fact, confirmed beyond doubt by experience, that even an approximately complete fixation of the colouring matter can only be brought about when the indigo is conveyed as such on to the fibre and then as rapidly as possible reduced and dissolved under conditions which prevent the alkali salt of indigo white from being washed away.

---

* *Persoz,* "Traité théorique et pratique de l'impression." Paris, V. Masson, 1846.

** English patent No. 3377, 1871. A similar process is described in the American patent No. 522042, 26. 6. 1894, by *Blanchon & Allegret.*

*** *Bancroft,* "Philosophy of Permanent Colours."

Fayence Blue Printing.

The first process founded on the principle of printing indigo itself, and dating about fifty years earlier than the solid blue process, is the so-called Fayence blue printing.* This process consists in printing the material with indigo in as fine a state of division as possible together with copperas or orpiment and a suitable thickening, and then hanging it in an alkaline solution. The indigo is reduced and dissolved at the same time, and in this condition dyes the printed parts. The method of carrying out the process is rather cumbersome, and is fully described by *Persoz* in the passage referred to. The Fayence blue process was certainly a remarkable advance compared with the processes then known, since the colour could be applied not only with a brush or hand block, but could also be printed on the roller printing machine, and thus allowed of the production of exact and delicate patterns previously unattainable. On the other hand, the method was complicated, uncertain, and costly. Dark shades could not be obtained by it, and although the principle, as afterwards shown, was correct, it had to give way to the solid blue process. The reason for this apparent contradiction lies in the fact that the process leaves out of account the second condition mentioned above for utilisation of the colouring matter, *viz.*, that the reduction must take place under such conditions that the alkali salt of indigo white will not be washed out. How this problem was solved in the course of time will be shown in the following chapters.

---

* *Persoz,* vol. III, page 59.

2. The Glucose Process.

a) Development of the Process.

Development of the Glucose Process.

Of all the different methods of direct printing of indigo on cotton fabrics, which have been employed, only the one based on the reducing properties of grape sugar has maintained its position. This "glucose process," as it is termed, is nowadays practically the only one used for printing indigo, and only in quite recent times with the introduction of formaldehyde-sulphoxylate (Rongalite C B. A. S. F. patent) has any rival really worthy of consideration arisen.

Grape sugar has been used since early times for the reduction of indigo; the honey vat so common in the Caucasus, and the American molasses vat are based on this reaction.

To *Bancroft* belongs the credit of having been the first to recognise the reducing property of sugar and molasses, and ascribe to it the reduction process in the honey vat,* while *Völker,* in a lecture delivered to the Academy of Sciences in Erfurt in 1816, seems to have been the first to declare with certainty that it is specially grape sugar that has this property.**

It is worthy of note that *Bancroft* had already recognised the value of sugar for indigo printing, and proposed to substitute it for the poisonous orpiment so much used at that time.

Nature of the oldest Methods of Indigo Printing: Applying reduced Indigo and preventing a premature Oxidation.

As shown in the previous chapter, the oldest indigo printing processes in all their different variations are based, with one exception, on the principle of applying the reduced indigo in the form of a thick vat or paste of indigo white to the fibre, and all attemps to improve these processes, whether by means of mechanical contrivances or by choosing suitable reducing or thickening agents, aimed first of all at preventing a **premature**

---

* Compare Experimental Researches concerning the Philosophy of Permanent Colours, etc., 1794, 2nd Ed.; translated under the title "Neues englisches Färbebuch" into German by *Buchner, Dingler* and *Kurrer,* Nuremberg 1817, vol. I, page 293.

** See *Bancroft*, "Neues englisches Färbebuch," page 293. The statement often met with, and also given in our Indigo Book (page 116), that *Fritsche* (1840) was the discoverer of the reduction of indigo with grape sugar is, therefore, not accurate. Compare also *Vitalis*, "Lehrbuch der gesamten Färberei," Weimar 1854, page 366.

oxidation of the dyestuff before printing. In this connection *Bancroft's* proposal also shows no advance, as he was still very far from the guiding principle of modern indigo printing, *i. e.*, printing the indigo as such, and carrying out the reduction on the fibre as a further stage by a special operation.

Nature of the modern Method of Indigo Printing: Applying the Indigo as such and preventing a premature Reduction.

Many years of practice have proved this method (first made use of in the so-called Fayence blue process), in which the prevention of a **premature reduction** is the important point, to be much the most advantageous, but the actual reason for this has not yet been actually ascertained. *William Jones Ward* of Manchester was the first to recognise that grape sugar above all is specially suited for carrying out this process, and in 1857 patented in England,* and the following year in France,** a process for printing indigo, which consisted in the employment of a reducing agent that did not attack indigo in the cold even in the presence of alkali, or only feebly attacked it, but reduced it on the fibre by subsequently steaming (or heating).

Ward's Glucose Process. 1857.

Grape sugar is named as the type of a reducing agent that fulfils these conditions.

Influence of the Temperature in Steaming.

The conditions, under which the steaming must be carried out, constitute a special feature of the process. In the description *Ward* indicates that the normal reduction of the indigo is favourably influenced by a steaming temperature of over 212° F., and claims expressly steaming with superheated steam, or under pressure, and a suitable apparatus for the purpose, as part of his invention.***

Freedom of the Steam from Air.

Ward had recognised and emphatically stated that the most important preliminary when steaming indigo prints is that the steam is completely free from air. It is also probable that he had actually worked according to his method with a steamer free from air, and had thus already fulfilled the most important condition for the success of indigo printing. This is shown by the correct observation that, other conditions being properly fulfilled, the most favourable time of steaming is the unusually short one of about 30 seconds.

---

* Letters patent No. 3038, A. D. 1857.

** French patent No. 37373, dated 18th July, 1858.

*** This portion of *Ward's* invention has recently been patented afresh in Germany. See German patent No. 122033, "Neuerung im Dämpfen von Indigodruck nach dem Glykoseverfahren" (Improvement in steaming indigo prints in the glucose process), *Kalle & Co.*, Biebrich a. Rh., and also Letters patent No. 9250 of the same firm.

The Part played by Alkali in Glucose Printing.

While *Ward* had thus recognised and described at least the most important features of the conditions for steaming, it is evident that he was not fully aware of the important part, which the nature and concentration of the alkali play in the printing colour, in fixing and utilising to the fullest extent the indigo present. His endeavour to mix with the printing colour as large a quantity of alkali (caustic soda and lime) as possible, suggests that he was conscious of the fact that the reduction of indigo during the steaming takes place with ease only when plenty of alkali is present; but he did not discover that the alkali in the printing colour, besides fixing the indigo, has a further important task to perform, and that in this case not the concentration, but the nature of the alkali is the chief consideration.

Ward designates glucose as a reducing agent which acts on indigo only feebly at the ordinary temperature. This description, however, can be applied to grape sugar only to a limited degree, as even at the ordinary temperature grape sugar reduces indigo in the presence of alkali. The rapidity of the reduction, whereby the printing colour is rendered useless, depends, however, (leaving the temperature out of the question) on the nature and concentration of the alkali in the printing colour. *Ward*, therefore, in order to preserve his printing colour as long as possible, decreased as much as possible the quantity of caustic soda by using a mixture of caustic alkalies with alkaline earths (milk of lime), which do not accelerate the reducing action so much as the caustic alkalies. Although this observation is quite correct in one respect, yet the weak concentration of the caustic alkali in the printing colour brings about another important defect.

Necessity of Mercerisation by means of the Printing Colour.

It is well known to every colourist who has anything to do with indigo printing (although the fact, so far as we know, has never been mentioned in technical literature) that the printed indigo, even when the conditions are otherwise suitable, is only imperfectly fixed unless the fibre has previously been mercerised by the caustic soda contained in the printing colour. On this account it must contain a much larger quantity of sodium hydroxide than is necessary for the preparation of the grape sugar-soda vat.

Leese's Printing Process.

The importance of this circumstance seems also to have escaped the attention of *J. Leese*, who worked out an indigo printing process with glucose about the same time as *Ward*, or a few years later, evidently independently of the latter. This process, based on the remarks of *Fritsche*[*] mentioned above, was identical with *Ward's*, and *Leese* was thus the first to reduce it to practice in Germany.[**]

Oxidation of the printed Goods.

Although *Ward* in the specification describes his process minutely and even with a certain verbosity, it is remarkable that he does not mention at all how the indigo white on the printed steamed goods is to be oxidised back to indigo blue, so that we cannot decide whether the goods were oxidised by hanging in the air or, as is usual nowadays, by washing in running water containing air. At all events, this latter method was used from the earliest times in the old processes of printing indigo[***] — brushed or painted blue, Fayence blue, solid blue.

a) with Water containing Air.

It would not strike one that any other method had been employed when first using the glucose printing process, if *Leese* had not expressly specified oxidation by exposure to the air or by dipping in an oxidising liquid, *e. g.*, a solution of sulphate of copper.

b) by Hanging and oxidising Agents.

However this may be, the glucose process as worked out by *Ward* and *Leese*, although it certainly represents an advance compared with the earlier processes, notably Fayence blue, does not fulfil the demands made by the printing industry for a process, which must be profitable in working and can be carried out with accuracy. The requirements clearly expressed by *Ward*, *viz.*, to prevent the reduction of the dyestuff during printing, and to bring it about on the fibre in a separate process, are not sufficiently fulfilled by the grape sugar in the *Ward-Leese* method of working, as described above, so that the faults inseparable from vat printing occur also in this form of the process, although not to so great an extent.

---

[*] Compare page 126, note.

[**] See Breslauer Gewerbeblatt, 1863, No. 7; Dingler's polytechnisches Journal, 1863.

[***] See, for instance, "A complete Discovery of the Cotton or Calico Printing previously kept so secret" (Karlsruhe 1768, published by *Mich. Maklot)*, anon., page 40, and *Kreyssig*, "Der Zeugdruck," Berlin 1844, vol. IV, page 321.

Development and Perfection of the Glucose Printing Process by Schlieper in 1870.

Adolf Schlieper showed how these defects also could be overcome by separating the reducing agent from the printing colour. According to his process, the fabric is padded with a solution of glucose, dried, and then printed with a colour consisting only of indigo, alkali and thickening. Only in this way is it actually possible to prevent a premature reduction of the dyestuff, to concentrate at will the alkali of the printing colour sufficiently for mercerisation, and, as the result of these advantages, to be able to utilise the dyestuff almost completely. This, however, does not exhaust *Schlieper's* share in the development and perfection of the process; this should be estimated rather by the fact that he ascertained most exactly all the conditions necessary for its success, and invented suitable apparatus for their fulfilment in practical working. He is thus the originator of those methods of carrying out the glucose printing process which are in use to-day, and the process generally, and rightly, bears his name. Messrs. *Schlieper & Baum* of Elberfeld have carried out since 1870 this modern form of the process as discovered by *Schlieper,* which was first made public in 1883 by a detailed description in the Bulletin de Mulhouse,* a description which has since then neither been changed nor added to.

J. Ribbert's Patent for a Glucose Printing Process.

Shortly before this publication *J. Ribbert* obtained a patent** for a similar process, not, however, so complete in its details.

In spite of the exact details being made known, *Schlieper's* process, requiring a special form of apparatus, was only slowly taken up, and was worked merely by a few large firms, though indeed on a very extensive scale. But simultaneously with the appearance of artificial indigo the exertions of the *Badische Anilin- & Soda-Fabrik* brought the process much more extensively into use, so that *Schlieper's* indigo printing process is employed to-day with the greatest success not only in the larger print works, but also by a number of smaller firms.

Extension of the Glucose Printing Process through the B. A. S. F.

b) Directions for carrying out the Glucose Process.

Directions for carrying out the Glucose Process.

We will now describe the conditions which must be observed for the successful working of the glucose process, that is, for a firm and complete fixation of indigo in the printed portions of the fabric as far as this is possible, and the reasons for them as based on the nature of the dyestuff and the reducing agent. In addition, this chapter sets forth the means, by which the necessary conditions are fulfilled on an industrial scale in the simplest manner.

---

* Bulletin de la Société industrielle de Mulhouse, 1883, vol. LIII, page 585.

** German patent No. 20368 of 7th October, 1881.

The various Operations of the Schlieper Process.

The *Schlieper* process consists of the following stages. The fabric is

1. prepared with a solution of grape sugar and dried,
2. printed with an alkaline paste containing indigo and dried again,
3. steamed,
4. oxidised and rinsed.

There are thus four different operations, reckoning each drying as part of the foregoing operation, and the details of these four stages will be described in detail in the following pages.

Preparation of the Goods with a Solution of Grape Sugar (Glucose).

Composition and Properties of Grape Sugar.

The glucose of commerce is a white hygroscopic mass, which has been poured while still in a fluid or semi-fluid condition into moulds and is brought into the market in blocks of about 50 lbs. weight. Its property of taking up water must be borne in mind when storing and handling. It is composed of reducing sugar, dextrine, water and small quantities of inorganic substances. The water and inorganic impurities are naturally absolutely valueless for the reduction of indigo; dextrine also exerts only a weak reducing action. The proportion of sugar present alone determines the value of the product, the commercial article containing on an average about 60 %. Grape sugar is very readily soluble both in cold and in hot water.

Concentration of the Solutions of Glucose used for Indigo Printing.

The most concentrated solutions of grape sugar are of a syrupy consistency, but these are never used for printing. Solutions of more than about 20° Tw., corresponding to $3^1/_2$ — 4 lbs. grape sugar per gallon, are never employed, and even this concentration was proposed only for a process described later on, in which the glucose serves not only to fix the indigo, but also to discharge an azo dyestuff developed on the fibre.*

---

* German patent No. 98796, process for white and colour discharges on Paranitraniline Red, etc., by *Schläpfer, Wenner & Co.*, Fratte di Salerno.

The quantity of grape sugar which must be applied to the material in the padding operation varies naturally with the strength of the printing colour. The darkest shades of indigo prints industrially produced require a colour containing 3 % of indigo. In a printing colour of this kind the indigo is utilised to the greatest possible advantage when the material is prepared with a glucose solution of 15° Tw., corresponding to 2½ lbs. glucose per gallon. But, on the other hand, such concentrated solutions have the bad effect of making the material too stiff, so that its further treatment is a matter of some difficulty. On this account a concentration of about 12° Tw., *i. e.,* about 2 lbs. grape sugar per gallon is generally considered sufficient.

When printing lighter shades alone, less concentrated solutions can be used. For medium shades padding with a solution of

9° Tw. = about 1½ lb. grape sugar per gallon,

and for pale shades with a solution of

6° Tw. = about 1 lb. grape sugar per gallon,

is sufficient.

When simultaneously printing several colours of varying shade, the strength of the glucose preparation must naturally be regulated by the darkest colour.

Handling and Storing the Solution of Grape Sugar.

As the grape sugar of commerce is occasionally slightly acid, it is advisable to add two or three drops of a solution of soda per quart till the reaction is neutral. Solutions of grape sugar should not be kept long, but should be used as fresh as possible, for they are inclined to ferment and become useless when stored.

Method of Working when preparing with Glucose.

For padding the goods *Schlieper* has proposed a specially constructed machine which differs from that usually employed by lengthening the passage through the solution in order to make sure that the material is thoroughly impregnated with it, but the employment of such a machine does not seem to be absolutely necessary, as experience has proved that the same effect is produced with the ordinary padding machine.

White goods may be worked at the ordinary temperature, though even in this case warm solutions of glucose are to be recommended, but mordanted or dyed material, which, as practice shows, is difficult to wet out, must be padded warm with glucose and, if necessary, several times. But whichever method is chosen, it is absolutely necessary that the goods should be completely impregnated with the glucose solution.

The pressure of the squeezing rollers must be so regulated that the goods take up their own weight of solution.

Drying the Prepared Goods.

With regard to drying the goods after padding, special care must be taken to avoid a high temperature, otherwise the goods become stiff and lose the elasticity necessary for their further working. At still higher temperatures, they turn yellow and the glucose partly loses its efficacy. On this account, glucose prepared fabrics should not be dried on the cylinder drying machine, but in a hot air drying apparatus (hot flue).

Fabrics prepared in this way acquire the property of the glucose of absorbing moisture from the air, and in this state offer a suitable soil for all kinds of bacteria and fungi and may become worthless through fermentation. For this reason the prepared material should be further treated as quickly as possible; preserving it for several days may lead to all sorts of annoyance (the production of stains) and uneven prints. It ought to be a rule that the treatment of prepared goods is continued at latest on the following day.

Additions to the Grape Sugar Solution.

To obtain special effects, other substances can be added to the glucose solution so long as they do not injuriously affect the development of the indigo. *Bloch* and *Schwarz*,* for example, have proposed treating the fabric with a mixture of grape sugar and naphthol, or other phenol, in order to produce by special methods insoluble azo dyes beside, or under, the indigo. The same authors recommend the addition of Turkey red oil to the grape sugar, as the blue is said thus to become fuller and brighter.

In our experiments we have not been able to confirm this result, and it seems to us that the addition of Turkey red oil to the solution of glucose has only value when its use is positively demanded for the simultaneous printing of other dyes, *e. g.,* Alizarines, with the indigo.**

---

* Compare "Couleurs azoïques, réserve sous impression de Bleu indigo vapeur," by *Bloch* and *Schwarz* in the Bulletin de Mulhouse, 1894, page 260.

** See the section: "The simultaneous printing of Alizarine dyes along with indigo, page 151."

Printing with Indigo.

The composition and preparation of the printing colours.

The Composition and Preparation of the Printing Colours.

The printing colour consists of indigo, thickening agent, and caustic soda, in addition to water. The quality and quantity of each of these components plays an important part in the success of the printing operation. With reference to the dyestuff itself, the first and most important condition for completely utilising the indigo is that it is in the finest and most even condition imaginable. As long as natural indigo was used for this purpose, the material had to be very carefully selected, in fact, many brands could not be sufficiently finely ground at all, and then the indigo had to be ground for several days with caustic soda to a sufficiently fine paste.*

Influence of the Fineness of the Indigo on its Utilisation.

Advantages of Synthetic over Natural Indigo.

All these difficulties disappear at once when synthetic indigo is used, but even with this product there are many differences in fineness, and not every synthetic indigo can be used without further preparation for printing. The various brands of Indigo pure B. A. S. F. all satisfy the highest requirements with regard to fineness.

Indigo in the form of paste can be employed without further preparation, but indigo powder must be made into an even paste by grinding for a short time with caustic soda.

Thickening Agents.

The proper selection of a thickening agent is also important. Starch alone cannot be made use of with such alkaline colours as indigo printing requires, as it becomes lumpy, owing to the action of the alkali, and prevents the preparation of a smooth thickening. In order to be worked up without trouble with caustic alkalies, it must be at least partially dextrinised. These conditions are more or less satisfied by the various brands of roasted starch. Pure dextrine is not suitable for indigo colours as it has not the necessary thickening property to bring the colour to the desired consistency, and because alkaline printing colours prepared with dextrine are very liable to run when steamed.

Dark roasted starch, mixed if desired with pure starch, has shown itself to be most suitable. Of all starches, maize starch and the British gum prepared from it by roasting, have the greatest thickening power, and these are recommended above all others by *Schlieper* and *Baum* in their publication already referred to. Occasionally flour is used. Printing colours made up in this way utilise the indigo to the fullest extent, but readily gelatinise when cold and must, therefore, be used warm.

---

* The difficulties to be contended with in grinding natural indigo sufficiently finely may be seen from the proposal of *C. Kurz* to dissolve indigo in aniline and then precipitate it, in order to secure it in a sufficiently fine state for printing purposes. Revue des matières colorantes, 1897, page 79.

Besides the flour and starch thickenings mentioned, gum is also used to a limited extent as a thickening agent. The alkaline gum printing colours do not utilise the dyestuff so completely as the starch printing colours, but on the other hand, especially in lighter shades, they produce more even and rather brighter prints. For this reason it is advisable to thicken with gum when printing large surfaces in light shades.

The Part played by the Alkali in the Printing Colour.

The third important component of the printing colour is caustic soda, and the correct proportion of alkali is of the greatest importance for the fixation of the greatest possible amount of indigo.

Grape sugar does not act on indigo in neutral solution or in the presence of alkaline carbonates, and this circumstance explains the fact that alkaline printing colours when stored in open vessels become useless. Free alkalies, on the contrary, and alkaline earths act energetically on glucose forming acids (chiefly lactic acid is produced from pure glucose), and experiments have shown that in this reaction 10 parts of commercial grape sugar fix approximately 3 parts of caustic soda. If this reaction takes place in the presence of indigo the latter is reduced to indigo white, at the same time going into solution.

Nature of the Alkali.

A difference exists between the action of the various alkalies on grape sugar, inasmuch as ammonia (which, however, being so volatile, is excluded from use for the present purpose), and quicklime act on it only feebly in the cold and only react strongly with it when heated to about 140° F., whilst caustic soda and caustic potash do so already at the ordinary temperature. Thus if indigo is added to a mixture of the latter kind, the reduction begins even in the cold; at a higher temperature, *e. g.,* about 212° F., it proceeds very rapidly and may in a comparatively short time lead to over-reduction and complete destruction of the dyestuff. It will be seen from the foregoing that the quantity of alkali contained in the printing colour must be sufficient to convert the grape sugar on the fabric com-

Amount of Alkali.

pletely into acid, at the same time neutralising it, and also to dissolve the indigo white which has been formed by the reduction of the dyestuff in the printing colour. For this latter purpose the amount required is comparatively small. A printing colour containing 3 % of the dyestuff does not need more than about 1/2 oz. of caustic soda (or the equivalent quantity of quicklime) per 100 oz. to dissolve the indigo white. Whilst this quantity, however, can be directly calculated, it is not possible in the same way to determine the amount of caustic soda which is fixed, when steaming, by the decomposition of the grape sugar, as this depends on several conditions, such as concentration of the glucose solution, thickness of the goods, pressure in padding, etc., which are constantly varying. But to get a general idea of this also, we have taken a typical case and by experiment and calculation have found* that with a fabric of medium weight, which had absorbed its own weight of a solution of grape sugar of 12° Tw., 6 oz. of caustic soda per 100 oz. printing colour were required for complete reaction with the grape sugar in the goods. According to this result, it should be expected that the alkalinity of a printing colour having 6 1/2 oz. of caustic soda per 100 oz. (*i. e.*, 6 oz. for the reaction with the grape sugar, and 1/2 oz. for solution of the indigo white) would slightly more than suffice to fix the indigo on the fibre.

Experience shows, however, that this is not the case, since the fixation, when printed, of the indigo with a colour containing 7 1/2 oz. caustic soda per 100 oz., the other conditions being favourable, is quite insufficient.

*Schlieper*** mentions that the proportion of caustic soda should lie between 29 and 31 1/2 oz. per 100 oz., and although our experiments have shown that such a hard and fast rule cannot be laid down as *Schlieper* supposed, yet it is certain that in order to secure the proper fixation of the dyestuff the concentration must be at least about three times as great as the amount calculated to be necessary.

---

* The experiment was carried out as follows: A piece of cretonne of known weight was padded with a solution of grape sugar of definite strength and then padded with indigo printing colour. The above figures were calculated after the padding from the increase in weight and the strength of the glucose preparation on the principle that "100 grams grape sugar correspond to 15 grams caustic soda."

** Bulletin de Mulhouse, 1884, page 54.

Mercerisation of the Material when printing.

This evident contradiction between theory and practice is fully explained by the following considerations. As is well known, the affinity of indigo white for cotton fibre is very feeble and in dyeing several dips must always be given to obtain fast dark shades. That is, if cotton is put into a concentrated vat it is certainly dyed deeply, but only a small quantity of the dye is actually fixed, and the greater part of it is completely removed by washing. Now, when printing indigo, which is really nothing but a dyeing of definite portions of the surface of the fabric, even dark shades must be dyed in one dip, and the printed portions of the material are impregnated with a concentrated vat. Under these circumstances, in spite of the complete reduction and solution of the dyestuff, it is not thoroughly fixed unless the absorbing power of the fibre has previously been sufficiently raised **by mercerisation.** But this is effected, as is well known, only by the action of highly concentrated caustic alkalies. With reference to the kind of alkali, it can thus be seen that the use of quicklime, which was formerly proposed by *Ward* for the production of stable printing colours, is not in the least rational, as it has no mercerising action. When printing indigo, the colourist is tied down to the use of caustic alkali. Just at what concentration in the printing colour, under the conditions of indigo printing, mercerisation occurs, cannot be accurately determined, as the action of the alkali on the fibre does not commence suddenly, but increases slowly with an increase of concentration. According to our experiments a noticeable deepening of the shade begins with an alkalinity of about 15 oz. per 100 oz. printing colour, and a powerful mercerising action sets in only with an alkalinity of over 20 oz. per 100 oz. Slight variations are produced by the nature of the thickening, more pronounced differences by the amount of colour conveyed on to the fibre, *i. e.*, by the depth of the engraving.

These circumstances must naturally be taken carefully into account when preparing the printing colour. In addition certain precautions must be observed in the composition of the alkaline thickenings in order to obtain an even mass with a good printing penetration. As a guide for the preparation of a starch thickening, a gum thickening, and a printing colour, we give the following examples, all of which have proved successful in actual practice.

Working Directions.

Alkaline Starch Thickening.

Preparation of the Alkaline Starch Thickening.

Make 6 lbs. dark burnt starch and
3 » wheat starch into an even paste with
1 gall. water. Then add with constant stirring
4 » caustic soda 90° Tw.

As the mixture becomes very hot on the addition of the caustic soda, and as the temperature should not exceed 170° F., otherwise the thickening becomes lumpy, the operation must be carried out in a jacketed pan, which can be cooled with water. For the same reason, the caustic soda should not be added all at once, but in small portions (which can be gradually increased) at a time. Further, care must be taken to stir very well. When all the caustic soda has been added, heat the thickening to 170° F. and maintain at this temperature, with constant stirring, for 15 minutes; then stir till cold. It is advisable to sieve the thickening before it completely cools, as it becomes thick when cold. A steel brush should be made use of, as the strongly alkaline colour destroys animal fibre. If the thickening, through want of attention, has become lumpy, the fault can hardly be remedied, and it is the best plan simply to throw it away.

Alkaline Gum Thickening.

Preparation of the Alkaline Gum Thickening.

Stir up 50 lbs. of a solution of gum Senegal (1:1) with
4 gall. of caustic soda 90° Tw.

The method of working is exactly the same as for the alkaline starch thickening, but the cooling must be even more carefully carried out, and the temperature should not rise above 80° F., otherwise the mass turns lumpy and so becomes useless.

Preparation of the Printing Colour.

To prepare the

Printing Colours,

the thickening is mixed cold with indigo in paste form,* and the mixture made up finally with caustic soda to the requisite consistency for printing. We give below examples of three typical printing colours.

---

* Indigo powder must first be ground to an even paste, see page 82.

Printing Colour for Dark Blue.

150	parts by weight	Indigo pure B.A.S.F. 20 %,
800	» » »	alkaline starch thickening,
50	» » »	caustic soda 76° Tw.
1000	parts.	

Printing Colour for Medium Blue.

100	parts by weight	Indigo pure B.A.S.F. 20 %,
850	» » »	alkaline starch thickening,
50	» » »	caustic soda 76° Tw.
1000	parts.	

Printing Colour for Light Blue.

50	parts by weight	Indigo pure B.A.S.F. 20 %,
900	» » »	alkaline starch thickening,
50	» » »	caustic soda 76° Tw.
1000	parts.	

The following may be given as examples of printing colours made with gum thickening and suitable for printing light shades in large designs:

I.	12	parts by weight	Indigo pure B.A.S.F. 20 %,
	988	» » »	alkaline gum thickening.
	1000	parts.	

II.	25	parts by weight	Indigo pure B.A.S.F. 20 %,
	975	» » »	alkaline gum thickening.
	1000	parts.	

III.	38	parts by weight	Indigo pure B.A.S.F. 20 %,
	962	» » »	alkaline gum thickening.
	1000	parts.	

Storage of the Printing Colour.

The strongly alkaline printing colour, when kept for a long time in an open vessel, absorbs carbonic acid from the air, and may thus become comparatively or entirely worthless, since alkaline carbonates do not react with grape sugar (see page 135). On the other hand, the printing colour, when kept in closed vessels, may be preserved indefinitely, and is even improved by long storing, a finer and more even distribution of the dyestuff in the mass taking place. For this reason it is advisable to store a supply of the printing colour for a long time in suitable vessels with a liquid seal, as shown in the sketch (Fig. 10). If the colour becomes gelatinous on keeping for a considerable time, this can easily be remedied by gently warming.

Printing and Drying.

Method of Printing.

Schlieper laid it down as a rule that for printing on the colour the material should be quite dry, the colour thick, and the pressure slight. All these precautions have the object of preventing as much as possible the penetration of the colour into the material and spreading it as a separate layer on the fabric, in order to prevent the alkaline colour mixing with the grape sugar, and thus causing a premature reduction of the indigo. For the same reason the drying after printing must be done at as low a temperature as convenient, if possible not above 85 ° F. Since only very little liquid is contained in the printing colour, drying the goods under the conditions mentioned can be performed without difficulty. Owing to the consistency of the printing colour, it is necessary to make use of an apparatus for brushing in while printing.

It need hardly be mentioned that woollen blankets must be avoided when printing indigo, as the strongly alkaline colour tends to destroy them; on this account india-rubber blankets are generally used. But it must be noted that the alkali which penetrates the goods may also unfavourably affect the back cloths in so far as that they become mercerised at such places, and thus have a greater absorbing property for all dyestuffs. As this undesirable effect does not disappear on cleansing, it may cause trouble later on when working up the goods, which served as back cloths, unless it has been fully taken into account.

Steaming.

Steaming.

The colour, which is very sensitive to moisture and the carbonic acid of the air, is spread, after printing, over a great surface, so that the goods in this condition are especially sensitive to unfavourable influences. The interval before steaming should, therefore, be as short as possible.

The following considerations, based on experience, will readily show which are the most favourable conditions for the steaming operation. The reduction of the dyestuff under the influence of grape sugar and caustic soda takes place completely only when the steam is almost entirely free from air, but if this condition is fulfilled, the reduction is effected almost instantaneously. The sodium salt of indigo white is taken up from its solution by the fibre, especially when mercerised, with extraordinary rapidity. These two properties permit of a very short steaming process, and on the other hand the printing colour has two properties which imperatively demand it. In the first place, caustic soda and grape sugar do not merely reduce indigo, but also very strongly attack it, so that by prolonging the steaming for only a short time much lighter shades are produced than correspond to the amount of indigo used. Secondly, the printing colours, owing to the large proportion of caustic soda present, are very hygroscopic and are, therefore, inclined to run. This inclination is intensified not only by the presence on the fibre of grape sugar, which is also hygroscopic, but also, and chiefly, because very damp steam must be used. Reduction does take place with fairly dry steam, but the indigo white produced in this case has not enough moisture to enable it to go into solution, and it remains in an undissolved state in the layer of printing colour on the fibre. In this way the dye has no opportunity of penetrating and being absorbed by the fibre, so that the actual dyeing process cannot take place. This causes not merely an insufficient exhaustion of the dyestuff, but also the disadvantage that the dye afterwards rubs off when washed, dissolving in the wash water and staining the whole of the goods.

The three indispensable conditions: **damp steam, free from air** and a **short steaming,** cannot as a rule be secured in the ordinary rapid steamer. *Schlieper* accordingly devised a special form of apparatus which fulfils the purpose admirably (Fig. 10 shows a diagrammatic sketch). Corresponding to the short period of steaming, the volume, as compared with the ordinary rapid steamer, is much less and the difficulty of obtaining a space filled with steam almost free from air is considerably lessened. With the same end in view the slits for the entry and exit of the goods are made as narrow as possible. As the steam is in most cases too dry for indigo printing, a special arrangement must be made to obtain the requisite humidity. This consists of a box placed below the rollers and filled with water, which is brought to the boil by means of a steam coil.

Over the surface of the water is arranged the steam coil for the direct current of steam. To prevent the goods from being splashed, there are three false bottoms inserted between the upper and lower parts of the apparatus, so arranged that their openings do not come opposite to one another. On account of the great quantity of damp steam, there is danger of the formation of drops, which is avoided by so constructing the heatable plate covering the steamer that it projects on the side where the goods enter, so that the moist steam rushing out strikes against the hot plate before it is removed by the suction apparatus arranged above the steamer. For the same purpose the slits for entry and exit of the goods are lined with heated copper tubes, so that condensation is prevented here also.

Before passing printed goods into the steamer, steam must be allowed to blow through the apparatus for some time, so that it may be thoroughly heated, and the air driven out as much as possible. When at work, the flow of steam must be so regulated that the temperature in the interior is fully 212° F., or better still about a couple of degrees higher. Under these circumstances the steam escapes in a strong stream out of the slit where the goods enter, and drives out of the material the air which would otherwise be brought into the apparatus. Printed goods should remain on an average about 45 seconds in the steamer. The colour of the print on leaving the apparatus should be yellowish brown. An olive colour points to incomplete reduction, and a pure yellow to insufficient moisture.

Oxidising and Washing.

Oxidising and Washing.

After steaming, the indigo on the fibre is in the form of an indigo vat, and in this condition the goods are sensitive only to drops of water. It has even been proposed to hang the goods for several days in the air in order to convert the indigo white into indigo. If the oxidation of the dye actually proceeded speedily enough in this manner, hanging in the air and afterwards removing the thickening would doubtless be the best method, because in this way the washing out of the indigo white and the consequent loss of dyestuff and other disadvantages would be avoided. Unfortunately, however, a complete re-oxidation of the indigo white embedded in the thickening is quite impossible in dry air, and even in moist air only after so long a time that this method could not find industrial application. The oxidation of the colouring matter must, therefore, take place simultaneously with the removal from the fibre of the substances which are of no further use, that is, in the washing machine. A little reflection will show here also the conditions which must be observed. The dyestuff is on the fibre in the form of the sodium salt of indigo white, which is soluble in water. Alkali and reducing agents are present in large excess, so that, when air and water are wanting, all the conditions required for the formation of a vat are fulfilled. To avoid this, the goods must be brought at once into contact with as much water as possible containing air. Any good open-width machine with a strong flow of water sufficiently satisfies these conditions. An arrangement has proved specially suitable, in which the waste pipe of the first compartment of the machine is placed at the bottom, so that the vessel cannot fill with water, and the goods on entering are thoroughly brought into contact with water and air by means of sprinklers at each side, if possible in several sets. The alkali and the unused glucose are in this way rapidly removed, and the indigo at the same time is oxidised.

Developing with the Aid of oxidising Agents.

It remains to be mentioned that when it is necessary to save water, this is best done by passing the goods, before bringing them into the washing machine, for a short time through an oxidising bath, preferably a solution of bichromate. The simplest method of arranging the necessary appliances is to fasten a small tub provided with a roller in front of the washing machine. This tub contains a solution of about 1 lb. bichromate per 100 gallons, and the level of the solution is kept constant by being fed from a reservoir placed at a higher level. The prints obtained by this method are, however, not so bright as those oxidised in running water alone. After passing once through the open-width washing machine, the thickening can be completely removed by washing in rope form in the usual way. The goods are finally well soaped and, if necessary, slightly chemicked.

Indigo prints prepared according to the glucose process are much faster to rubbing and washing than indigo dyeings of the same shade, owing to the mercerisation of the fibre.

3. The Printing of Indigo with Maltose.

Printing of Indigo with Maltose.

Maltose is very similar to glucose in its chemical behaviour, but there are certain differences in the reducing action of the two substances. As we ourselves have shown,* this variety of sugar may be employed in indigo printing according to exactly the same method as glucose in spite of these differences. Maltose is not a commercial article like glucose, the solutions must be prepared on the spot from starch. This is, however, an exceedingly simple matter, for, under the influence of malt and the diastase contained in it, starch splits up into one-third dextrine and two-thirds maltose. The crude maltose solutions thus obtained may be employed directly for padding the material. The addition of the sugar to the printing colour is inadvisable also in the case of maltose, since this substance, like glucose, reduces indigo in the cold in the presence of alkali.

The conversion of starch into sugars can be brought about still more easily and safely than with malt or infusions of malt by means of the malt extract put on the market some time ago by the *Deutsche Diamaltgesellschaft* of Munich, under the name "Diastafor." When this product is employed, the method of treatment is as follows:

Directions for the Preparation of a Maltose Solution.

Preparation of Maltose Solution.

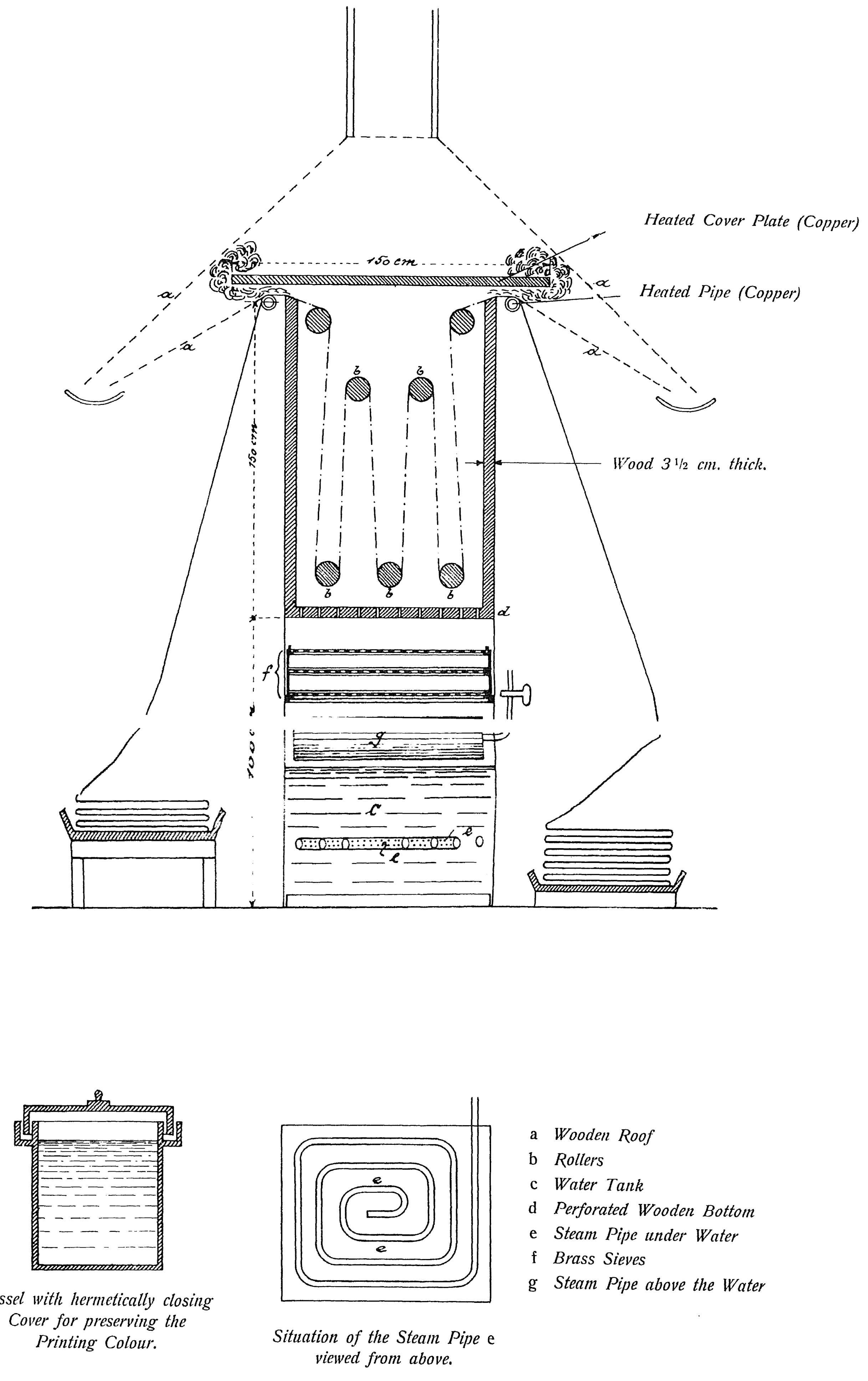
Boil up 100 parts of wheat starch with water to a thin paste, and after cooling to 140—160° F. (a higher temperature is unfavourable to the action of the diastase) convert it into sugar by adding 2 parts of Diastafor. The wheat starch may be replaced by other kinds of starch without materially altering the result. When the conversion into sugars is complete, which is usually the case after 3—4 hours, and is recognised by the absence of the blue starch reaction with iodine, the solution is made up to 10° Tw., and the fabric is padded with it.

With regard to the method of printing, the details given in the previous section with reference to glucose printing also apply when maltose is employed.

---

* Letters patent No. 6495 (1905).

Steaming Apparatus for Indigo Printing.



ssel with hermetically closing Cover for preserving the Printing Colour.

Situation of the Steam Pipe e viewed from above.

a Wooden Roof
b Rollers
c Water Tank
d Perforated Wooden Bottom
e Steam Pipe under Water
f Brass Sieves
g Steam Pipe above the Water

Fig. 10. Steaming Apparatus for Indigo Printing (after Dépierre).

4. The Printing of Indigo with other Carbohydrates.

Printing of Indigo with other Carbohydrates (Dextrine).

Ward, in the patent referred to on page 127, mentioned among the reducing agents, which might be used for printing indigo according to his process, besides the various sugars dextrine and similar substances. He stated further that for successful working of the process the steam must be free from air, and is preferably superheated. *Ward's* discovery was destined to be completely forgotten in the course of time, and it has happened, just as in the case of glucose printing, that indigo printing with other carbohydrates was re-discovered independently by various persons and at different times after the introduction of our synthetic indigo had aroused considerable activity in this branch of printing. We ourselves were the first to do this,* shortly afterwards *P. Wilhelm,*** and subsequently others,*** took out patents referring to this process.

None of the later publications contain anything novel compared with *Ward's* original process. The method has not been able to make headway on the practical scale, chiefly because not all dextrines or partially dextrinised starches are equally suited for the reduction of indigo. In some cases the reducing action, like that of dextrine itself, is too weak, so that too long a steaming is necessary; in other cases, owing to the presence of glucose, it is too strong, and vats are formed in the printing colours, even in the cold. The process has for this reason been viewed with considerable distrust. That it is, however, better than its reputation, and can be carried out in practice under suitable conditions, is best shown by the fact that several printworks are accustomed to produce pale and medium blues, generally in combination with other colours, with printing colours containing indigo and an alkaline roasted starch thickening without any previous preparation of the material. It can, therefore, hardly be considered superfluous if we give directions for carrying out a process of this kind.

---

* Compare French patent No. 278376 of 1898, not completed.

** Bulletin de Mulhouse, 1901.

*** German patent No. 123607 and Letters patent No. 9587 (1900).

Directions for the Printing of Indigo with Dextrine as Reducing Agent.

Printing of Indigo with Dextrine.

Apart from the necessity for a suitable continuous steamer, the success of the process depends chiefly on the choice of the right kind of British gum. Of all the varieties known to us we find British gum No. 2 of the firm *F. von der Heide,* Hilden, Germany, to be the best adapted for this purpose.

Printing Colour.

Stir up 16 lbs. British gum No. 2 with
16 » (13 pints) water. Then add
$6^{1}/_{2}$ gall. caustic soda 70—76° Tw.,
$2^{1}/_{2}$ lbs. Indigo pure B. A. S. F. 20 $^{0}/_{0}$,
2 » glycerine.

After printing, dry thoroughly, steam 2 minutes in the indigo steamer, and wash, etc., as described under glucose printing.

5. The Printing of Indigo with Formaldehyde-sulphoxylate (Rongalite C patented).

a) General Remarks.

Printing of Indigo with Rongalite.

As may be gathered from the foregoing sections, all the reducing agents hitherto described, hydrosulphite as well as carbohydrates, conform only to a limited extent to the essential requirements of an indigo printing process that they should leave the colouring matter unaltered even in the presence of strong alkalies at the ordinary temperature, but reduce it rapidly and without loss when steamed. Either their reducing power is too weak, as in the case of the dextrines, to convert the colouring matter rapidly enough for practical purposes into a form capable of dyeing, or, like the hydrosulphites and the sugars, they bring about this change at the ordinary temperature, so that in the one case there is loss of colour and unsatisfactory results, in the other inconvenient complications in the method of working.

Only quite recently have reducing agents been discovered, which are superior to any hitherto known, both with respect to their indifferent behaviour in the cold and their effectiveness at the temperature of the steaming operation. We refer to the formaldehyde-sulphoxylates,* and of these compounds the most suitable for indigo printing is the sodium salt on account of its ready solubility in water and caustic alkalies; this is placed on the market by the *Badische Anilin- & Soda-Fabrik* under the name Rongalite C patented. This product in its action resembles hydrosulphite in so far as it converts indigo almost instantaneously and without loss into indigo white, but is fundamentally distinguished from hydrosulphite by the fact that at ordinary temperatures and in the presence of alkalies this reaction only takes place very slowly and incompletely. In consequence it is possible to add the reducing agent directly to the printing colour and thus avoid the complication of a previous preparation of the material. Otherwise with regard to the method of working the principles mentioned in connection with glucose printing apply equally to printing with Rongalite with the exception that the conditions in steaming are not quite the same. As previously stated, when indigo is reduced with glucose a considerable and rapid destruction of the colouring matter takes place if the steaming operation is prolonged beyond the length of time absolutely necessary. This danger is not present in the case of Rongalite. The conditions are similar to those occurring when indigo is reduced with hydrosulphite,** and the time of steaming may, therefore, be longer. Since, however, the printing colour, owing to its strong alkalinity tends to run, the steam must be in this case perfectly dry. If this requirement is fulfilled, the steaming may be considerably prolonged, and the ordinary rapid ager may be employed, provided that it is sufficiently free from air, a condition, which in many of the older agers could only be attained after running for some time, but in the modern agers, as constructed for discharge printing with formaldehyde-sulphoxylate, can be brought about at all times. The complete removal of air from the interior of a modern ager of this kind may be effected with a comparatively small consumption of steam by arranging for the admission of steam at the top of the ager, so that the air contained in the apparatus or brought in with the goods is driven out at the bottom. (In the older machines the steam entered below and, rising in consequence of its lower specific gravity, mixed with the air in the interior.) The openings, by which the goods enter and leave the steamer, are at the bottom. A sketch of an ager of this kind will be found in our pamphlet on Rongalite.

---

* Compare *Baumann, Thesmar, Frossard,* Bulletin de Mulhouse, Nov. 1904, and *Reinking, Dehnel, Labhardt,* Berichte der deutsch. chem. Gesellschaft, 1905, page 1069, and the corresponding Letters patent No. 13 955 (1904).

** Compare page 87.

Owing to the possibility of adding the reducing agent to the printing colour and of carrying out the steaming operation in a machine in general use for other purposes also, the application of Rongalite considerably simplifies the printing of indigo. Since, however, the prolongation of the time of steaming is only possible at the expense of a less complete utilisation of dyestuff than in the glucose process, the advantage of the Rongalite method is chiefly apparent in its application for pale and medium shades.

b) Instructions for Printing.

Instructions for Printing with Rongalite.

The proportion of Indigo paste 20% to Rongalite should be approximately 2:1. For dark shades the amount of Rongalite may be somewhat increased, for pale shades, where the reducing effect of the thickening is appreciable, slightly diminished. An excess of the reducing agent is just as much to be avoided as an insufficiency, since the former renders the oxidation difficult and furthers the removal of indigo white in washing. If, however, the correct proportion of Rongalite to indigo is taken, the oxidation takes place more readily than in glucose printing, and does not demand such perfection in the washing machine, because the effectiveness of the reducing agent is destroyed by steaming, and the danger of vat formation in the washing machine is lessened.

The **general** formula for a Rongalite printing colour is illustrated by the following:

Colour for Dark Blue.

100	parts	alkaline thickening,
20	»	Indigo pure B.A.S.F. 20%,
10	»	Rongalite C.

The Rongalite is dissolved in the indigo paste by warming, and the mixture well stirred together with the thickening; for pale shades the colour is correspondingly reduced.

The remarks made with regard to glucose printing apply to this process also. The drying before steaming can, however, be carried out at a higher temperature and even on drying cylinders. The length of time for steaming when using moist steam is 30—40 seconds, but with dry steam may be increased to 4—5 minutes.

Pattern No. 5.

Indigo print with Rongalite.

Pattern No. 6.

Indigo print with Rongalite.

6. The Printing of Indigo on Animal Fibres.

Printing of Indigo on Animal Fibres.

In the preceding section it was pointed out and explained that the reduction of indigo with carbohydrates takes place with regularity only in the presence of large quantities of free alkali, and it is evident that printing with the aid of these substances is not practicable on the animal fibres owing to their sensitiveness to alkali. Rongalite and hydrosulphite, however, reduce indigo not only in weakly alkaline, but also in neutral or even acid media. It is also the case that indigo white is soluble not only in alkalies, but also (as shown for example in the letters patents Nos. 22402 [1900] and 1159 [1901] already referred to), though to a considerably less extent, in weakly alkaline salts of the alkali metals, and in substances such as glycerine. The possibility of mercerisation is absent in the case of animal fibres, nor is this effect necessary, since the affinity for indigo white is much greater. In spite of this, the presence of alkali is necessary, at any rate in printing dark shades, to bring the indigo into complete solution, and a slight excess above the theoretical amount, still keeping below the quantity injurious to the fibre, considerably improves the brilliancy of the blue. Another fundamental difference compared with the printing of cotton is that a premature reduction of the colouring matter does not lead in the case of animal fibres to incomplete fixation and great loss of dyestuff. It is, therefore, possible to print on wool and silk with thickened vat liquors. An exceedingly suitable product for this purpose is, for example, our Indigo vat B.A.S.F. 60 %, which contains just sufficient alkali to dissolve the colouring matter, and thus ensures that no excess is present. Of course, indigo itself may also be employed with the addition of the requisite amount of caustic soda.

By taking these facts into account, printing colours for wool and silk may be prepared which have no injurious action on these fibres.

Printing Instructions.

Printing Colour for Silk.

Instructions for printing Indigo on Silk and Wool.

Prints on animal fibres require a considerable amount of moisture when being steamed, and in order to furnish this moisture it is advisable to make use partly or wholly of the following very hygroscopic

Glycerine Thickening.

Make 400 parts by weight British gum,
200 » » » water,
400 » » » glycerine

into a paste, and heat to 160—180° F., keeping at this temperature for 15 minutes and stirring well.

Printing Colour.

$11^{1}/_{2}$	parts	Indigo vat B.A.S.F. $60\,^{0}/_{0}$,
100	»	glycerine,
610	»	glycerine thickening,
30	»	Rongalite C,
$48^{1}/_{2}$	»	water,
200	»	gum thickening 1:1.
1000	parts.	

Print, dry, steam 4—5 minutes, and rinse.

Printing Colour for Wool.

150	parts	Indigo pure B.A.S.F. $20\,^{0}/_{0}$,
100	»	caustic soda 70—76° Tw.,
650	»	glycerine thickening,
90	»	Rongalite C,
10	»	turpentine,
1000	parts.	

Print, dry, steam 4—5 minutes, and rinse.

7. The Printing of Indigo along with other Dyestuffs.

Printing of Indigo along with other Dyestuffs.

It is, of course, only possible to print indigo along with colouring matters which can be fixed upon the fibre under the same conditions as indigo itself. The number of such products

Indigo pure B. A. S. F. / *R*. Indigo pure B. A. S. F. / *G*.

is unfortunately very limited. Firstly may be mentioned the few derivatives of indigo which find practical application, *viz.*, monobromindigo (Indigo pure B.A.S.F. / *R*) and tolylindigo (Indigo pure B.A.S.F. / *G*). The former yields a redder and brighter, the latter a duller and greener shade than indigo. They differ from the parent substance only by being rather less soluble in alkali, but more readily reduced. They may be printed according to any of the processes already described, either alone, mixed with indigo, or beside indigo.

Printing of Indigo along with Indanthrene.

Much the same conditions apply in the case of the Indanthrene dyestuffs as for the true indigo colouring matters. Although the indigo printing processes are not the most favourable for the Indanthrenes, yet they may be printed quite satisfactorily by these methods. The combination with Indanthrene Blue especially is rational and practical. There is such a great difference between the fastness to light of pale and dark shades of indigo to the disadvantage of the former that the substitution of indigo by Indanthrene Blue, which is comparatively faster to light, in the pale shades is highly to be recommended. This substitution is further assisted in the case of the glucose process by the fact that Indanthrene Blue fixed in this manner does not exhibit its usual characteristic bright shade, but a much duller shade similar to indigo. Pattern No. 7 illustrates a combination of this kind.

Pattern No. 7.

Indanthrene with indigo. Glucose process.

Combination of Indigo Printing with other Dyestuffs.

For the sake of completeness it may be mentioned that the sulphur colours can also be fixed according to the methods used in indigo printing. Up to the present, however, combinations of this kind have acquired no technical importance.

A further possibility of combination is afforded by those colouring matters, which withstand the action of strong alkalies and reducing agents even at high temperatures. The number of such products is very small, and Aniline Black is the only one of practical importance. The combination is effected by first printing and developing the black, and then printing a "cover" of indigo over it by whichever process is preferred.

The difficulties are much greater when a design has to be formed not by cover printing over a black already developed, but by simultaneously printing of black along with blue, since the development of the black is a process of oxidation in an acid medium and is prevented by the action of reducing agents and alkalies. Of course, the less the black is exposed to these influences, the less difficulty will be met with. Patterns should be avoided in which the black and blue colours touch, or blurred edges will certainly occur, and patterns should be chosen in which the indigo can be fitted in. The printing of Aniline Black along with indigo, when the latter is printed according to the Rongalite process, offers no special difficulty if contact of the alkaline colour with the black already printed can be avoided. Aniline Black, moreover, in the case of a special style, which will be described later on, can be printed on glucose prepared material by suitably modifying the printing colour. Since this subject belongs more to the domain of Aniline Black, and has been fully treated by *W. Triapkine,** a mere reference to it will here suffice. The albumen colours can be combined with indigo, when working according to the Rongalite process, as readily as Aniline Black. The printing of Aniline colours along with indigo has scarcely been attempted, obviously owing to the great difference in fastness, there is no great demand for such combinations. The azo colours produced on the fibre form an exception. *Bloch* and *Schwarz*** have shown that colours of this kind may be produced along with indigo by a mixed preparation of the fabric with glucose and beta naphthol. As far as we know this process has not been adopted in practice. Recently, however, indigo has been printed with Rongalite along with insoluble azo dyestuffs for shirting styles. A process of this kind — Indigo and Para Red — is illustrated by pattern No. 8. The indigo is printed according to the Rongalite process as given on page 148, the azo colouring matters are produced by the usual methods.

---

* *W. Triapkine,* Rongeage de rouge turc par la méthode alcaline. Paris 1899, page 70.

** Compare page 133.

Pattern No. 8.

Indigo and Para Red.

Printing of Indigo along with Alizarine Colours.

The printing of Alizarine colours along with indigo is a problem, which has often been investigated, but only quite recently satisfactorily solved. The experiments in this direction were unsuccessful so long as it was sought to adapt the fixation of indigo to the methods in use for Alizarine colours.* The *Badische Anilin- & Soda-Fabrik* succeeded in overcoming the difficulty by a process** in which the reverse course is adopted. It has been found that, although on glucose prepared material the Alizarine dyestuffs printed in the usual way are not developed by the short steaming necessary for the reduction of the indigo, yet they are sufficiently well fixed to withstand the washing required for oxidation. Their complete development then follows in a second steaming process corresponding to the usual steaming of Alizarine colours, which in turn does not injuriously affect the indigo. For this process the material is prepared with the mixture of glucose and Turkey red oil which has been recommended for other purposes.* The process is generally applicable for Alizarine colours, and is now carried out in several printworks. The same principle can, of course, be applied to Rongalite printing.

---

* Compare German patent No. 123608 and Letters patent No. 7779 (1899).

** Compare Letters patent No. 6094 (1903).

Directions

for printing Indigo along with Alizarine Red.

Prepare the goods with a solution of

2 lbs. glucose
$^1/_2$ lb. Turkey red oil
a few drops of ammonia
} per gallon of water,

dry, and print with the following colours:

a) Indigo

150	parts	Indigo pure B. A. S. F. 20 %,
850	»	thickening S.
1000	parts.	

b) Alizarine Red

Stir	150	parts	Alizarine GFX 20 % with
	520	»	starch thickening, add
	80	»	acetate of lime 15° Tw.,
	75	»	Turkey red oil D,
	80	»	sulphocyanide of alumina 32° Tw., and
	95	»	lactate of tin 45° Tw., and mix thoroughly.
	1000	parts.	

After printing, the indigo is first fixed as described under the glucose process; the material is then again steamed, this time for one hour without pressure or half an hour at 7 lbs. pressure, then washed and lightly soaped.

When the indigo is printed by the Rongalite method, the goods are prepared with a 10 % solution of Turkey red oil only. Directions for the Indigo-Rongalite printing colour will be found on page 148. The printing colour for Alizarine Red and the other details of working remain the same. Instructions for producing Alizarine colours other than red will be found in our work on "The Alizarine Colours of the Badische Anilin- & Soda-Fabrik," pages 52—101.

---

* Compare page 133.

8. Resists under Steam Indigo Blue.

Resists under Steam Indigo Blue.

It has been already mentioned on page 119 that acids and oxidising substances possess the property of precipitating indigo and indigo white from their solutions. If substances of this kind are printed in a suitable way on fabrics which are afterwards dyed in the vat, their presence brings about an increased depth of shade owing to a precipitation of colouring matter in the fibre as long as the precipitating substances are present in or on the fibre in a highly diluted condition. They produce, however, quite a different effect when a certain limit of concentration is exceeded; in this case the precipitation of dyestuff occurs before the solution can penetrate the fibre, and no dyeing takes place.

In addition to this, the purely mechanical action of the thickening and the undissolved substances in the printing colour, which form a dividing layer between the print and the material, oppose to a greater or less degree, according to the nature of these substances, the fixation of the indigo.

When goods, therefore, which have been printed in this way with a resist, are coverprinted with indigo according to one of the foregoing processes, the fixation of the indigo is prevented in the places printed with resist, and the cover falls away.

Oxidising with Sulphur.

Sulphur may be mentioned as a type of the class of substances which have an oxidising effect on indigo and, therefore, prevent reduction on steaming. *Schlieper* proposed sulphur as the best agent for the purpose in his first description of his printing process already referred to.* To produce coloured resists the sulphur may be combined with other suitable substances. Yellow, for example, is obtained by the addition of cadmium chloride to the printing colour, this on steaming forms yellow cadmium sulphide on the fibre. Similarly acetate of alumina may be added to the sulphur resist with the result that by the combined action of drying and steaming sufficient alumina is deposited on the fibre to permit of a subsequent dyeing in the usual manner with mordant dyes, *e. g.*, with Alizarine Red. In this manner also other coloured resists

Coloured Resists.

---

* Bulletin de Mulhouse, 1883, pages 586 and 602.

may be obtained which can be fixed by drying and short steaming and are not affected by sulphur.

Partial Resists.

Partial resists (pale blue or dark blue) are obtained by the addition of caustic soda to the resist, which renders the glucose partially inactive.

The process first proposed by *Schlieper* in this form has been adapted to a certain extent industrially.

Colouring the Resists with Substantive Dyestuffs.

Colouring with Azo Colours produced on the Fibre.

More recently it has been attempted to combine the sulphur resist with direct colours and with the azo colours developed on the fibre. *Bloch* and *Schwartz** have shown, however, that the substantive colours cannot be fixed in a sufficiently fast form under the conditions of glucose printing. Trials with the azo colours produced on the fibre also yielded unsatisfactory results, for although the formation of these colours is not prevented by the sulphur the shade is considerably affected.

These experiments on the production of azo colours under indigo were continued by *E. Colli,*** who attempted to replace the sulphur wholly or partially by other resisting agents having less influence on the formation of the azo colours. He specially recommends a lactic acid resist, which, according to his statements, yields useful results at least for white resists. It has been shown, however, elsewhere*** that lactic acid alone, like other organic acids, furnishes no results of practical value.

Resist Process of J. Ribbert.

Of very recent date is the process of *J. Ribbert*† of Hohenlimburg, Germany, who makes use of the paste of gum, acids, and oxidising salts which is employed as a resist for vat blue.†† This process, which is protected by patent, is easily carried out at any rate for white resists. In consequence of the physical condition of the resist, which only permits of the production of large patterns, it serves for an entirely different style of design from the sulphur resist and is scarcely suitable for employment alone but preferably in combination with a resist process under a dyed vat blue.

---

* Bulletin de Mulhouse, 1894, page 260.

** Bulletin de Mulhouse, 1902, page 424, and 1903, page 210.

*** Bulletin de Mulhouse, 1902, page 428: "Report on *Colli*'s work" by *Jul. Brandt,* and 1903, page 215: Report by *R. Bruckmann.*

† German patent No. 163 276: "Process for the production of white and coloured indigo resist styles."

†† *G. Tagliani* describes his experience with the metallic salts usually employed in resist printing in the Zeitschrift für Farben- und Textil-Chemie, 1903, page 333.

Discharge Resists under Steam Blue on previously coloured Grounds.

It may be mentioned finally that discharge resists analogous to the discharge resists under dyed vat blue* have been proposed for glucose printing on previously dyed grounds. Such resists destroy the dyed blue in the printed portions and at the same time prevent the fixation of the indigo printed as a cover.** They may be prepared with red prussiate of potash which destroys the indigo of the ground and the printing colour as soon as the alkali in the latter acts upon it. This process yields the same effect as the discharge printing, described on page 175, in the so-called "double style" which is produced by dyeing over a glucose print and then discharging. We have not heard, however, that such discharge resists are actually in use in practice.

Directions for Printing.

Directions for printing with Sulphur Resist.

It is essential if the sulphur is to resist sufficiently that it is in as finely divided a condition as possible. Flowers of sulphur are not sufficiently fine, and milk of sulphur must therefore be used.

Printing Colour.

500 parts	milk of sulphur,
500 »	gum thickening 1:1.
1000 parts.	

If the indigo is to be fixed by the glucose or maltose process, this resist colour is printed on the prepared material, or, if the Rongalite process is employed, on the unprepared cloth.

After printing, the material is thoroughly dried and cover printed or padded with indigo according to any desired process. Dark cover prints are only resisted with sulphur with difficulty, and for this reason the use of the process is almost exclusively confined to the production of pale shades.

---

* Compare the section on this subject, pages 201 and 212.

** Compare Revue génér. des mat. colorant., 1903, No. 83, page 322.

9. The Printing of Indigo with simultaneous Discharge of Aniline and Alizarine Grounds.

a) General Remarks.

Printing of Indigo with simultaneous Discharge of Aniline and Alizarine Grounds.

Concentrated caustic soda has the property not only of dissolving many metallic oxides and compounds used as mordants for material to be afterwards dyed, but also of destroying certain finished dyeings, and by virtue of these properties may be employed as a discharging agent. One of the most largely used dicharge processes for basic colours, *viz.*, that discovered by *Felix Binder,** depends on the action of concentrated caustic soda. From what has just been said it is evident that the process may be carried out in either of two ways. Either the tannin mordant, which is chiefly used for fixing colouring matters of this class, is destroyed by printing with caustic soda, so that on dyeing the colour will not be fixed in the discharged portions, or the dyeing itself may be destroyed. Both methods of working are in use, but as a rule the former is preferred owing to the greater purity of the discharge effects which it yields. Since all indigo printing colours for cotton fabrics must contain very concentrated alkali for the reasons described in Section IV, and since also the discharge is effective under the conditions and in the time necessary for steaming indigo prints, and the action is not disturbed by the presence of reducing agents, it is possible to produce with any desired indigo printing colour prints with a blue discharge pattern on a ground dyed with basic colours. In our pattern-card No. 252 "Indigo pure B. A. S. F. in its application for tannin discharge styles" special directions are given for this process. The conditions are similar in the case of Alizarine colours on alumina mordant, and here also the discharge may be printed either on the mordant or on the finished dyeing. Only discharge printing on Turkey Red is of practical importance, but for this style both variations of the alkaline method are employed to a considerable extent. Discharge printing on a mordant was discovered by *A. Schlieper* and first described at the same time that the glucose process was published.**

Discharge Printing on Alizarine Red Mordant.

---

* Bulletin de Mulhouse, 1900, page 93.

** See page 130.

The printing of indigo is carried out in the same way as usual, but the dyeing process for Alizarine Red, both with regard to the mordant and the actual dyeing operation, must in this case be considerably modified. For discharge printing on the mordant the most suitable process consists in impregnating the material with aluminate of soda and Turkey red oil, thus depositing an alumina lake on the fibre, then printing with the discharging indigo colour, and afterwards dyeing in as short a time as possible and at a comparatively low temperature with the addition of lime and Turkey red oil to the dye-bath, finally oiling and steaming. The shortening of the time of dyeing is essential for the production of a pure blue. The red is only developed in the final steaming. The above process requires very careful manipulation, but is carried out on a large scale in many printworks.

Discharge Printing on finished Alizarine Red.

Schlieper also suggested a process for the discharging of finished Turkey red; this was subsequently modified and improved by *J. Schmidtlin* in such a way that his process is worthy of a place beside *Schlieper's* first invention. The *Schmidtlin* process has been minutely described by *W. Triapkine** and we do not propose to describe it in detail here. We can only mention the principles according to which in this process the indigo is fixed on the fibre. Although dyeings with trioxyanthraquinone, which are yellowish in tone and less resistant, are discharged by caustic soda alone, dyeings with dioxyanthraquinone — Alizarine itself — are not sufficiently discharged, so that instead of white a more or less deep violet results, or on printing with indigo an unsightly reddish shade of blue. This difficulty has been removed by adding silicate of soda to the printing colour and also giving a passage through a silicate solution after steaming. The effect of the alkaline silicate is completely to convert even a red, which is most difficult to discharge, into soluble substances. Indigo is employed in this style not only for blue but also for green in combination with Chrome Yellow. The lead required for this purpose is brought on to the fibre by the addition of plumbate of soda to the printing colour. Blue is seldom produced alone on the red ground by means of alkaline discharge printing, but is nearly always combined with white, yellow, and black besides green. In the production of these colours the presence of a reducing agent is, however, not only unnecessary, but with yellow and black actually injurious, since in the former case it hinders the fixation of the lead, in the latter the development of the black.* By employing the Rongalite process in place of the glucose method an improvement may also be effected in this case.

---

* *Triapkine,* "Rongeage du Rouge turc par la méthode alcaline." Masson & Cie., Paris 1900. Compare also *H. Schmidt's* remarks regarding this book. Lehne's Färberzeitung, 1900, page 128.

We have up to now considered those cases, in which the dyestuff is destroyed by the alkali. With other classes of dyestuffs the reducing agent, assisted it may be by the caustic soda, is the destructive agent. This is the case with all the azo colouring matters, and of these the colours produced on the fibre, notably Para Red, are of most importance for our purpose. Discharge printing on Para Red was carried out by *Züblin* and *Zingg*** according to the glucose process by making use of glycerine, which dissolves Para Red at the temperature of steaming, and thus renders easy its destruction by the glucose. Since the introduction of Rongalite it must be said that this process is now entirely superseded, since it is possible to work with Rongalite in a much simpler and more certain way. Rongalite-indigo printing colours intended for discharge printing on Para Red and similar colours only differ from those intended for simple indigo printing by containing an increased proportion of Rongalite corresponding to the twofold task of the reducing agent.

b) Indigo on Turkey Red.

Discharge Printing on Mordant.

1. Mordanting.

Discharge Printing on Turkey Red Mordant.

The material is thoroughly boiled out and rinsed, then padded with a solution of

75 parts aluminate of soda 20° Tw. } 18° Tw.,
25 » Turkey red oil F }

and carefully dried at 100—120° F. The mordanting bath may be used continuously.

---

* Compare page 153.

** German patent No. 98796, expired.

2. Fixing.

The alumina is fixed by a 10 minutes' passage through a cold solution of

1 part ammonium chloride in
100 parts water.

The fixing bath must be renewed each time.

After passing through this solution, the goods are carefully rinsed.

3. Printing of Indigo with simultaneous Discharge of the Mordant.

The material is printed with indigo either according to the glucose or the Rongalite process, the printing colours and methods of working being the same as those already described.

4. Dyeing.

The dye-bath is prepared with

3 lbs. Alizarine 20 % } per 100 gallons water
1 gall. clear lime water } of 5° hardness.

The boiling water is poured over the Alizarine paste, and the lime then added. The temperature of the dye-bath should be 175—195° F., the material should be well turned in the bath for 3 minutes, taken out, and thoroughly washed.

5. Oiling.

After rinsing, the goods without drying are padded with a mixture of

10 parts Turkey red oil,
90 » water,

and then dried.

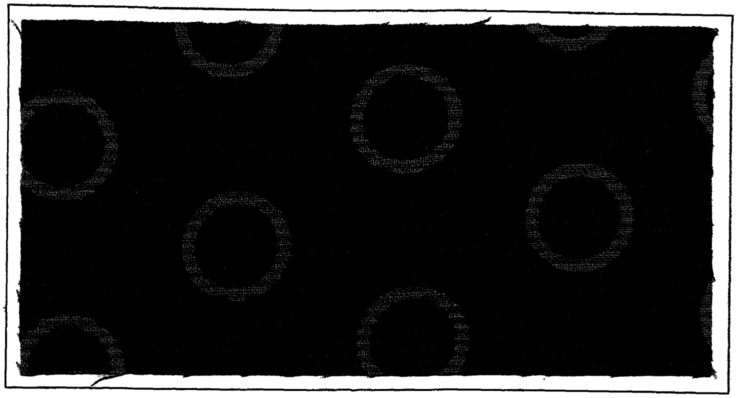
6. Steaming

then takes place for 1 hour at 7 1/2 lbs. pressure.

7. Brightening.

The goods are finally soaped boiling for 1/2—1 hour with 5 lbs. soap per 100 gallons water, rinsed, and dried.

Pattern No. 9.



Indigo on Turkey Red.

Discharge print on mordant (*Schlieper's* process).

Discharge Printing on finished Turkey Red.

Discharge Printing on Turkey Red.

By making use of *Schmidtlin's* process it is possible to discharge satisfactorily any kind of Turkey Red, but with respect to the ease with which the Alizarine lake is split up and converted into soluble products great differences exist, depending on the nature of the colour lake. A red dyed according to the aluminate of soda process is most readily discharged. The process is carried out as follows for blue and green.

The material is padded with a solution of glucose at 10—12° Tw. Since the red cloth does not wet out very easily, it is advisable for the sake of an even prepare to pad twice, and to use the glucose solution warm.

Printing Colour for Blue.

20	parts	Indigo pure B.A.S.F. 20 %,
77	»	alkaline thickening S,
3	»	silicate of soda 76° Tw.
100	parts.	

Printing Colour for Green.

45	parts	alkaline dextrine thickening,
40	»	lead solution,
10	»	silicate of soda 76° Tw.,
5	»	Indigo pure B. A. S. F. 20 %.
100	parts.	

Alkaline Dextrine Thickening.

37 1/2 lbs.	dextrine	made into a paste, heated to 160° F., and stirred for 1/2 hour at this temperature.
6 1/4 gall.	caustic soda 106° Tw.	

Lead Solution.

400	parts	nitrate or acetate of lead,
520	»	water,
80	»	glycerine.
1000	parts.	

After printing, the goods are steamed 3/4 minute, hung up in the air for several hours, washed, and passed for 1/4—1/2 minute through a boiling bath of silicate of soda at 1 1/2—2° Tw. They are then soaped, rinsed, chromed at 120° F. with 2 lbs. bichromate and 1/4 pint hydrochloric acid per 10 gallons water, and once more washed.

When Rongalite C is the reducing agent, the glucose prepare is dispensed with, and the following colours are used:

Discharge Colour for Blue.

15	parts	Indigo pure B. A. S. F. 20 %,
8	»	Rongalite C,
74	»	alkaline thickening S,
3	»	silicate of soda 76° Tw.
100	parts.	

Discharge Colour for Green.

40	parts	alkaline dextrine thickening,
40	»	lead solution,
5	»	Indigo pure B. A. S. F. 20 %,
2 1/2	»	Rongalite C,
12 1/2	»	silicate of soda 76° Tw.
100	parts.	

The method of working is the same as when glucose is used except that the alterations in steaming for Rongalite prints, described on page 147, must be made in this case also.

Pattern No. 10.

Discharge print on Turkey Red with glucose (*Triapkine's* process).

c) Discharge Printing on Paranitraniline Red and Alpha-naphthylamine Claret.

The material dyed in the usual way with Para Red or Naphthylamine Claret is printed with the following

Discharge Printing on Paranitraniline Red and Alpha naphthylamine Claret.

Discharge Colour for Blue.

150	parts	Rongalite C	dissolved warm and then cooled down.
150	»	Indigo pure B. A. S. F. 20 %	
700	»	alkaline thickening	

After printing, the goods are steamed for 2 minutes, washed, and soaped.

V.

Indigo Discharge Printing.*

1. The chemical Principles underlying the Discharge Process.

In the foregoing section certain processes were described by means of which a previously dyed colouring matter is destroyed by the action of caustic soda, and indigo fixed at the same time. It is evident from the conditions under which indigo is printed on the fabric that it is not attacked by alkalies alone. This is also the case with acids, at least under conditions which are not injurious to the fibre, and in so far as they do not possess an oxidising action. It is, therefore, not possible to discharge indigo with acids or alkalies. In calico printing use is also made of the action of reducing and oxidising agents to destroy colouring matters on the fibre. Indigo is chemically changed by the action of both these classes of substances.

Transformation under the Influence of Reducing Agents.

Under the action of reducing agents indigo is converted into indigo white. This transformation takes place with especial ease when alkalies are present to dissolve the indigo white. It has been pointed out, however, in preceding sections that only when hydrosulphites and sulphoxylates (Rongalite) are used does the reaction take place without considerable loss, and that with other reducing agents the reduction proceeds to a greater or less extent beyond the formation of indigo white, and produces other substances, which vary according to the nature of the reducing agent, the temperature, and the quantities taken, these substances having no longer the character of colouring matters or the property of becoming re-converted into indigo on exposure to air. It must be acknowledged that we only know with certainty the fact of the loss of colouring matter, and that at present we have no more exact knowledge regarding these products arising from the so-called over-reduction than we have of the actual phases of the process of reduction.*

---

* While this book is going to press we are preparing "A process of discharge printing with **Rongalite** for practical use." Please refer to our special directions.

Reduction Discharge.

Even with glucose and alkali it is possible to completely destroy indigo on the fibre. Still more energetic is the action of reducing agents in the presence of acids. Even hydrosulphites and formaldehyde-sulphoxylate (Rongalite), which cause a scarcely appreciable loss in alkaline reduction, destroy considerable quantities of indigo when used in neutral or acid solution. The power of reduction to destroy colouring matters is made use of in calico printing in the tin and zinc dust discharges, and both these methods of discharging give results with indigo which indicate the possibility that they may eventually find employment in connection with this dyestuff.

Tin Discharge.

In the tin discharge stannous salts — stannous chloride or acetate — are the effective agents. The composition and method of application of the discharge colour for indigo does not differ from that generally used for other purposes. On account of the more stable nature of the dyestuff the time of steaming must be comparatively long, and this fact greatly strengthens the usual objection to the tin discharge, *viz.,* the danger of tendering the fibre.

Zinc Dust Discharge.

The zinc dust discharge consists of a thickened mixture of bisulphite with a large quantity of zinc dust, and its action is based on the formation of hydrosulphite. This is, however, not to be understood in the commonly accepted sense that the discharging action is due to the hydrosulphites formed when the zinc dust is added to the bisulphite. These are destroyed for the most part during the preparation and storing of the discharge colour, and the decomposition is completed during the drying after printing, *i. e.,* before they can exert any action on the indigo. The only hydrosulphite which can have any discharging effect is that which is formed afresh during steaming from the neutral sulphite and the zinc dust remaining over from the first formation of hydrosulphite; this is decomposed immediately, and continues to be regenerated as long as any zinc dust remains present. The powerful effect, greater than that of ready prepared hydrosulphite, is to be explained by its acting while in the nascent condition. The composition of the colour suitable for discharge printing on indigo differs from the usual zinc dust discharge colour only by an addition of acetine, upon which the action on indigo largely depends. The zinc dust discharge does not attack the fibre, but has the disadvantage that it cannot be printed on machines, because the zinc dust sticks in the engraving of the printing rollers.

---

* Compare *A. Binz,* Chem. Industrie, 1903, page 248. Zeitschr. f. Elektrochemie, 1903, pages 599, 809. Zeitschr. f. angew. Chemie, 1904, page 40.

Both kinds of reducing discharge are of special interest, because they permit of the production of coloured discharges by the direct addition of Aniline colours, which is not possible with other discharge processes for indigo. Directions for the discharging of indigo with tin crystals will be found in our process No. 698 and the corresponding pattern-card No. 979, and for the zinc dust method of discharging indigo in the German patent No. 97 593.

Transformation under the Influence of Oxidising Agents.

That the reducing discharges have not found practical application is explained by the fact that by adoption of the opposite principle, *viz.,* by oxidation, the desired end is more simply and safely reached. Indigo is converted by oxidising agents, both in the presence of alkalies and of acids, into isatine. This product, which is only slightly coloured, is easily soluble in alkalies, and sufficiently so in hot water and dilute acids to allow of its being completely removed from the fibre by means of the usual washing operation.

Oxidation Discharge.

Thanks to the exertions of various leading colourists several methods for discharging indigo by means of oxidising agents have been devised, which are among the most ingenious processes of calico printing, and it is these only which find practical application at the present time. The method of working varies greatly according to the oxidising agent employed. The various processes are based on the application of chromates and potassium ferricyanide either alone or in combination with chlorates. Hypochlorites in the form of the chloride of lime vat, as first proposed by *D. Köchlin*[*] for discharging Turkey red, were also used for a time. The proposal of *Persoz*[**] to use gaseous chlorine for discharging indigo has not found practical application, nor have several processes based on the use of other oxidising agents* (alkaline chlorates, manganese peroxide, lead sesquioxide, permanganate, and nitric acid) had more than a temporary practical importance. Naturally, we can only treat in these pages of those processes which are industrially applied at the present day.

---

[*] Compare *Persoz*, vol. III, pages 53 and 234.

[**] Compare *Persoz*, vol. III, page 53.

2. The Chromate Discharge.

a) General Remarks.

Chromate Discharge. Thompson's Process.

The oldest known attempts to discharge indigo date from the first quarter of the last century. *Thompson,* a Manchester manufacturer, was the first to succeed in working out a practical process.** His process consisted in impregnating the dyed fabric with bichromate, and then printing with an acid discharge containing tartaric and oxalic acids, and, for heavy patterns, a little nitric acid also. The chromic acid liberated in the printed portions destroys the indigo even in the cold, or in any case when the temperature is slightly raised in drying. When the chromic acid has yielded up its oxygen, the excess of acid is removed by washing in running water, or by a passage through a hot chalk bath. Partial discharges due to incomplete destruction of the indigo are obtained by using citric acid alone.

This method of working has many defects; owing to the sensitiveness to light of the material prepared with bichromate, direct sunlight must be entirely excluded. The quantity of bichromate necessary is also very large, but in spite of this the amount which is really effective is so small that only pale shades can be discharged satisfactorily. Nor were these defects overcome by a variation of the process, in which the material was printed with the thickened acids before passing it through the bichromate bath. *Thompson's* process has, therefore, been completely given up for white discharges on indigo alone. *Thompson* himself did not employ it at first for discharge printing on indigo, but for producing designs on a fast green consisting of quercitron dyed on an indigo ground. If the fabric is mordanted with alumina before the preparation with bichromate, or if basic aluminium sulphate is added to the neutral chromate solution, so that alumina is precipitated on the fibre on drying, its presence in no way hinders the discharging action. The mordant will be dissolved by the acid discharge paste and removed from the fibre on washing, so that when the material is afterwards dyed with quercitron or fustic the design remains white. In this, its original form, *Thompson's* process is still now and again employed when the presence of green in the indigo is necessary. A similar effect can be obtained in no other way.*

---

* A brief description of all these processes will be found in *Dépierre,* "Traité de la teinture et Impression," vol. III, page 388.

** Bulletin de la Société Industr. de Mulhouse, vol. I, page 83.

Camille Köchlin's Process.

The chromate discharge first acquired its outstanding importance in the form given to it by *Camille Köchlin* in 1869. This process consists in printing the bichromate on the material, and then passing through a warm mixture of sulphuric and oxalic acids. In this manner even the darkest blues can be discharged to an excellent white. The further extension of the process for the production of coloured discharges is also due to *C. Köchlin.* If, instead of the acid chromates, the neutral salts are employed, albumen and acid resisting colours or colour lakes may be added to the discharge pastes without causing a coagulation of the albumen, which only occurs simultaneously with the discharge effect during the passage through acid, and the pigments are thus satisfactorily fixed.

Production of Coloured Discharges.

Another kind of coloured discharge with a natural dyestuff was mentioned by *Köchlin* himself. If an indigo dyed fabric is padded with catechu and then printed with the discharge, the brown colour is fixed by oxidation on the discharged portions, and is removed from the blue parts of the material by the subsequent operations. The direct production of coloured discharges with Aniline colours has hitherto been found impossible, since there are no dyestuffs suitable for coloured discharges, which sufficiently withstand the powerful oxidising action in the presence of warm acids. Better results are obtained, as *Elbers* has shown,** by the production of azo colours on the fibre, the material being prepared with beta-naphthol before printing, and the diazo solutions added to the discharge paste. *Elbers* only succeeded in producing a red with amidoazobenzol, all other diazo solutions proved insufficiently resistant to the action of bichromate. It has, however, been shown by others that paranitrodiazobenzol may also be employed. *Lauber* has described* a roundabout method of producing Para Red, according to which it is said even dark blues can be satisfactorily discharged, which cannot be effected by *Elbers'* process. All these processes have the defect that it is not possible to produce a white along with the red on the blue ground, since under the influence of the oxidising discharge the beta-naphthol, with which the fabric is prepared, gives rise to brown substances, which cannot be removed from the fibre. *C. Kurz* and *F. Kunert*** have striven to remove this defect by padding the material with a mixture of neutral sodium chromate and naphtholate, and printing simultaneously, for white with lead acetate alone, and for red with lead acetate mixed with paranitrodiazo solutions. Insoluble lead chromate is thus formed on the fibre, in the latter case along with the red colouring matter. If the material is now washed with dilute ammonia, both the excess of soluble sodium bichromate and the sodium naphtholate are removed, and in the passage through acid, which follows, the blue is discharged by the lead chromate still on the fibre. Apart from the technical difficulties, which render it nearly impossible to carry out this process practically, it possesses the disadvantage that by far the greater portion of the sodium chromate is not utilised, and it is, therefore, very expensive. This defect is avoided, but the technical difficulties are even greater, when instead of producing the insoluble chromates on the fibre they are printed direct on material which has been dyed and prepared with beta-naphthol, and the excess of naphthol washed away from the fibre after printing. It may be maintained without exaggeration that hitherto no variation of *Köchlin's* process has attained the practical importance of the original method of working. The chromate process as carried out by *Köchlin* is employed on a very large scale for white and coloured discharges on indigo dyed grounds.

---

* A detailed description will be found *Persoz,* Traité, etc., vol. III, page 384.

** German patent No. 55779, expired.

It has not only been attempted to improve the colouring of chromate discharges, but various alterations in the method of working have been suggested. Since these proposals are based

---

* Handbuch des Zeugdrucks, vol. II, page 233.

** *Lehne's* Färber-Zeitung, 1897, page 49.

Chemistry of the Chromate Discharge.

upon the chemistry of the discharging action we will devote a few words to this subject. Immediately after the publication of *Thompson's* process *D. Köchlin* [*] put forward the explanation that the acid which is printed on the fabric liberates chromic acid from the chromate and this chromic acid destroys the indigo. This explanation of the reaction is correct but not complete, because the action is affected by the nature of the acid which liberates the chromic acid. In all methods of working which are applicable in practice oxalic acid forms a part of the acid. The common explanation that the oxalic acid renders harmless the excess of oxidising agent is at best only a part of the truth. Its presence is an indispensable condition for the attainment of a good discharge effect, for, without it, the destruction of the indigo is incomplete. In this case also we only observe the fact, we cannot find an undisputed explanation of the actual course of the reaction. Of the various attempted explanations that of *Schaposchnikoff* [**] appears to us to be the most probably correct, namely that the chromic acid does not attack the indigo at once, but first oxidises the oxalic acid according to a well known reaction, and that the oxygen thus set free at the moment of its liberation destroys the indigo. The details of this explanation will be found in the publication referred to.[***] All the experiments of the various investigators have only led to one certain conclusion, *viz.*, that the oxalic acid cannot be replaced by any other agent with even approximately the same good result, and that a considerable quantity of this acid must be taken in proportion to the sulphuric acid to ensure a smooth working of the discharge process. The cost of the process is chiefly determined by the quantity of oxalic acid used. The discussion of the part played by the oxalic acid in the chromate discharge has led in recent times to attempts to diminish the consumption of oxalic acid by mixing it in the form of an alkaline or better a lime salt with the discharge paste.* The technical possibility of such a method cannot be gainsaid, but since it does not entirely do away with the addition of oxalic acid to the cutting bath, this process as far as we are aware has not been largely adopted.

---

[*] Bulletin de Mulhouse, vol. I, page 83.

[**] Compare *Buntrock,* Zeitschrift für Farben- und Textil-Chemie, 1902, page 459.

[***] With regard to the part played by oxalic acid in discharging compare also *Mullerus* and *Margulies,* Lehne's Färberzeitung, 1892/93, page 284; *Georgievics,* Zeitschrift für Farben- und Textil-Chemie, 1903, page 199; *Jorrissen* and *Reicher,* Chem. Zeit., 1902, page 1174; *Prud'homme,* Revue gén. des mat. col., 1903, page 65; *Newjadomsky,* Chem. Zeit., 1904, page 423.

Experiments have been made with chromates other than those of the alkali metals; these offer no advantage of any kind over the chromates of the alkalies for simple discharge printing, but may be employed with advantage in the discharge resists which will be described later on among the resist processes. In these discharge resists a colour is printed on a light blue ground which not only has to discharge the indigo at a later stage of the process, but also has to prevent the printed portions from taking up colour when the fabric is afterwards dyed in dark shades. If soluble salts were used in this case they would be dissolved out in the vat and the colour would lose its discharging power. Neutral or basic chromate of lead, which may be produced on the fibre itself, or chromate of zinc** is used for such purposes. The latter has the recommendation that of all insoluble chromates it is the most readily decomposed by acid.

Behaviour of Indigo R and G in the Chromate Discharge.

The foregoing remarks regarding the chromate discharge refer only to indigo itself and do not apply to its substituted derivatives Indigo R and Indigo G. With these products the chromate discharge is excluded inasmuch as no satisfactory white discharges are to be obtained with it under practical working conditions. The reason for this is different in the two cases. Tolylindigo (Indigo G) is much more resistant to the action of oxidising agents than ordinary indigo, and a complete destruction of the colour is thus rendered difficult. Bromindigo (Indigo R) on the contrary is oxidised to para-bromisatin, but this product is considerably less soluble in acids and in water than ordinary isatin, so that it cannot be completely removed from the fibre either by the acid bath or by washing, and dyes the material yellow. A better result can be obtained in the case of the halogen derivatives of indigo by adding minute quantities of certain salts, *e. g.,* vanadates, to the discharge paste. Since, however, these two brands have not been introduced to any great extent in cotton dyeing, methods of discharging them are not yet of practical importance.

---

* Compare Rev. gén. des mat. col., 1903, page 65; *Bulard,* 1904, page 257; *Sünder,* 1906, page 3.

** *Lehne's* Färber-Zeitung, 1902, page 128.

Disadvantage of the Chromate Discharge.

Our description of the chromate discharge would be incomplete if we did not refer to the disadvantages appertaining to it as well as to its advantages. In the acid bath the effect of oxidation is not only to destroy the indigo, but also to convert a portion of the fibre into oxycellulose. This undesirable tendering of the fibre can never be entirely avoided, and if an excess of chromate has been used the action may be so vigorous that the fabric in the printed portions becomes completely rotten. The whole fabric may also be tendered in the same way and made rotten if it remains too long in the hot acid bath. Owing to the solubility of oxycellulose in alkalies the tendering of the fibre is most noticeable after the goods have been washed in soap and soda and may then often be observed even when the formation of oxycellulose has been so slight that tendering can scarcely be perceived in the finished goods, as long as they are new. It is often possible to ascertain whether a discharge effect has been produced with chromate or by the chlorate process to be described later by testing the difference in strength before and after washing. It is, therefore, advisable to avoid the printing of heavy patterns or stripes with a chromate discharge. In the case of fine, disconnected patterns the tendering of the fibre can be so reduced by proper working that, as proved by the widespread employment of the chromate discharge, it becomes a negligeable quantity.

Protecting Additions to the Chromate Discharge.

Many attempts have been made to protect the fibre from the action of the chromic acid not utilised in destroying the indigo by adding substances to the acid bath which are more difficult to oxidise than indigo, but more easily oxidisable than the cotton fibre. Among such bodies, for example, are glycerine, the use of which was proposed by *H. Köchlin,* and alcohol suggested by *Brand;* others have proposed to add thickening agents, molasses, grape sugar, and even silicate of soda. This question has been carefully examined by a competent authority* and a favourable action recognised in the case of certain additions. This action extends in fact beyond the protection of the fibre to the prevention of attack on the indigo ground by the chromic acid present in the acid bath when working continuously. For this reason protective substances of this kind, especially gum or some other thickening agent, are occasionally added to the acid bath, but they do not find general application.

---

* *A. Scheurer,* Bulletin de Mulh., 1891, page 487; 1892, pages 278, 281, 540.

It must be mentioned finally that differences in the dischargeability of dyeings produced in different kinds of vats* are said to have been observed according as the alkali in the vat is lime or caustic soda, but in the light of our own experience we cannot confirm this statement.

Chromate Discharge on Wool and Silk.

Experiments have also been made to employ the chromate process for discharging indigo dyed wool and silk. The destruction of the colouring matter takes place satisfactorily on animal fibres although an increased quantity of chromate and a longer immersion in the cutting bath are required. The difficulty, however, occurs that the isatin thus formed, by reason of its acid character, and the great affinity of animal fibres for substances of all kinds, cannot be sufficiently removed by the ordinary washing operation, so that the discharged patterns possess a dirty yellow colour. By introducing after the acid bath a bleaching operation with sulphurous acid, hydrogen peroxide, etc., this defect may be removed. Processes of this kind for white and coloured discharges are described in German patents Nos. 118 287, 121 142, and 122 265 (all of which have expired) where the detailed method of working will be found. The production of coloured discharges is simpler in the case of animal fibres than with vegetable fibres, since the number of available Aniline colours possessing sufficient resistance to the action of the discharge is larger. Owing to the lack of demand for such styles these processes have not acquired any great technical importance.

b) Instructions for Discharging with Chromates.

Instructions for the Chromate Discharge.

The series of operations is as follows: Printing the cloth, drying, passing through the cutting bath, washing, and drying. We commence our description with the preparation of the discharge paste.

The consistency of the discharge paste naturally varies according as it is to be employed for printing with rollers, perrotine, or block printing. The choice of thickening agent also depends on the method of printing. For machine printing as a rule thicker pastes are employed than for perrotine or block printing. For two-sided discharges, which are but seldom required, and can only be produced satisfactorily on thick material, thicker pastes are used and additions, such as glycerine, which tend to assist the penetration, are avoided.

---

* Compare *Dépierre,* vol. III, page 417.

The directions given below for discharge work refer to machine (roller) printing, since this is the most important branch of discharge printing. The quantity of the discharging agent is regulated according to the depth of the blue ground and the nature of the engraving of the roller. On the latter factor as well as on the quality of the fabric, and the degree of penetration required, depend the choice of thickening agent and the consistency of the printing paste. It is, therefore, impossible to give recipes capable of universal application, and the printer must determine in each case the conditions which best suit his purpose.

In the case of the so-called "double style" mentioned on page 158, the amount of chromate must be varied in proportion to the dark blue previously printed.

White Discharge on Medium and Dark Blue.

600	parts	light roasted starch thickening,
40	»	ammonia,
130	»	bichromate of soda,
230	»	water.
1000	parts.	

The bichromate is dissolved in water, neutralised with ammonia, and mixed with the thickening. The whole is then warmed with constant stirring, cooled down still stirring continuously, and strained.

If the greatest possible degree of penetration is desired, an addition of glycerine is made.

Thickening.

500 parts light roasted starch and
500 » water

are mixed at first cold, then brought to the boil, and again cooled with continuous stirring.

To show the limits, within which the composition of the discharge paste may be varied, we give for comparison a

White Discharge for Pale Blue for Two-sided Prints.

770	parts	light roasted starch thickening,
20	»	bichromate of soda,
10	»	ammonia,
200	»	water.
1000	parts.	

For coloured discharges such colouring matters must be added as resist the oxidising action of the chromic acid and are not affected by the acid of the cutting bath. Pigment colours of this kind are placed on the market ready for use (*G. S. Siegle & Co.,* Stuttgart; *Fabriques de Produits Chimiques de Thann et de Mulhouse,* Mülhausen, Alsace).

Yellow Discharge on Medium Blue.

300	parts	starch-tragacanth thickening,
50	»	bichromate of soda,
80	»	water,
20	»	ammonia,
40	»	Chrome Yellow paste $60\,^0/_0$ *(Fabr. de Prod. Chim. de Thann et de Mulhouse),*
15	»	egg albumen solution (1 : 1).

The first four components are boiled together with constant stirring, then stirred until cold, and the Chrome Yellow and albumen stirred in.

Starch-tragacanth Thickening.

80	parts	wheat starch,
200	»	water,
200	»	gum tragacanth ($6\,^0/_0$),
600	»	water,
20	»	olive oil

are boiled together and stirred until cold.

Albumen Solution (1 : 1).

1000	parts	egg albumen,
1000	»	water,
25	»	turpentine,
25	»	ammonia

are mixed together cold and well stirred after solution is complete.

Yellow Discharge on Pale Blue for Two-sided Prints.

395	parts	light roasted starch thickening,
10		bichromate of soda,
5		ammonia,
90		water,
400		Chrome Yellow paste,
100		egg albumen solution (1:1).

Orange Discharge

is prepared in the same way as the yellow discharge described above, using Discharge Orange paste (*Fabriques de Produits Chimiques de Thann et de Mulhouse*) instead of the Chrome Yellow paste.

Discharge Paste for Green.

To produce a green discharge, a mixture of Chrome Yellow and Prussian Blue may be employed, the proportions of the two colours being varied according as a yellowish or bluish green is desired, or a ready prepared discharge green, which is a commercial product, may be taken.

The following printing colour gives a bright yellow shade of green:

230	parts	starch-tragacanth thickening (see previous [page]),
70		bichromate of soda,
200		water,
20		ammonia,
50		glycerine

are stirred together and warmed, cooled down still stirring, and then

120	parts	Prussian Blue paste 60 %,
220		Chrome Yellow extra fine paste *(G. Siegle & Co., Stuttgart)*,
130		Chrome Yellow S paste *(G. Siegle & Co., Stuttgart)*

are added, and finally

80	parts	egg albumen solution (1:1)

are stirred in.

A fuller and bluer shade of green is obtained with the following printing colour:

380	parts	starch-tragacanth thickening (see page 177),
60	»	bichromate of soda,
20	»	ammonia

are stirred and warmed together, and after cooling down

390	parts	Discharge Green *(Fabr. de Prod. Chim. de Thann et de Mulhouse),*
150	»	egg albumen solution (1:1)

are added.

Blue Discharge for Dark Blue.

(For the production of light blue designs on a dark blue ground.)

With this discharge colour an addition of albumen is unnecessary.

220	parts	tragacanth thickening 6 %,
60	»	bichromate of soda,
20	»	ammonia,
100	»	water

are warmed and stirred together, and after cooling down mixed with

600	parts	Discharge Blue *(Fabr. de Prod. Chim. de Thann et de Mulhouse).*

Red Discharge for Dark Blue.

320	parts	starch-tragacanth thickening (see page 177) or British gum thickening,
60	»	bichromate of soda,
20	»	ammonia,
100	»	water

are warmed and stirred together, allowed to cool, and

400	parts	Discharge Red EN *(Fabr. de Prod. Chim. de Thann et de Mulhouse),*
100	»	egg albumen (1:1)

are then added.

Pattern No. 11.

White and coloured chromate discharge.

The coloured discharges described up to the present all contain as the colouring agent pigment colours, the fixation of which in most cases depends upon coagulation of the albumen in the hot acid bath. A very brilliant red, which is also very fast to washing, can be obtained with an azo colour produced on the fibre according to the following directions:

Nitrosamine Red Discharge on a Medium Blue.

The indigo dyed fabric is padded with the following naphthol solution:

150	parts	beta naphthol are dissolved in
150		caustic soda 70° Tw. and
2000		water at about 120° F., then
500		Turkey red oil are added, the whole filtered and made up with
7200		cold water to
10000	parts.	

The material, after padding, is dried at about 100° F.; the drying operation must not be prolonged or stains will result. The discharge printing colour is prepared as follows:

I.	800	parts	Nitrosamine Red 25 % are diluted with
	2000	»	cold water, then
	370	»	hydrochloric acid 15° Tw. are stirred in. After standing for ½ hour the whole is filtered and made up with
	330	»	cold water to 3500 parts.

Separately

II.	700	parts	bichromate of soda are dissolved in
	5500	»	British gum thickening 1:2,

and the solution I is stirred into the paste II.

The printing colour must be used as quickly as possible, and cannot be preserved for subsequent use.

Further Treatment of the printed Goods.

The material is dried at 100° F., and during drying is protected from light as far as possible. It is then passed through an acid bath containing

5 lbs. oxalic acid and
5 » sulphuric acid 168° Tw.

per 100 gallons. The length of the passage is ½—2 minutes, and the temperature 120° F. A longer passage or a higher temperature should be avoided owing to the risk of tendering. The cutting with acid takes place in a lead-lined vessel containing guide rollers; the pieces are passed through in the open width and immediately afterwards, by means of sprays and running water, are thoroughly washed to effect the complete removal of the acid.

Printing a Discharge and simultaneously Resisting an Aniline Black Cover Print.

According to this process, white or coloured designs may be produced along with black on an indigo ground, the method consisting in adding to the discharge paste an alkali, which prevents the development of the Aniline Black. The order of operations is as follows: Printing the discharge resist, drying, cover printing with Aniline Black, steaming, passing through the discharge bath, rinsing, and after-treatment with soda.

Discharge Resist for White.

700	parts	British gum thickening (1:1),
80		bichromate of soda,
220		caustic soda 76° Tw.

Discharge Resist for Yellow.

300	parts	British gum thickening (1:1),
50		bichromate of soda,
150		acetate of soda,
50		soda,
100		water

are warmed and stirred together, and after cooling down an addition is made of

150	parts	Chrome Yellow paste,
200		egg albumen solution (1:1).

Discharge Resist for Red.

300	parts	British gum thickening (1:1),
20		bichromate of soda,
130		water,
150		acetate of soda,
50		soda.

To the mixture, when cold, are added

150	parts	Discharge Red powder,
200		egg albumen solution (1:1).

The pieces printed with the discharge resist are dried in the usual manner, and cover printed with the following Aniline Black colour:

100	parts	wheat starch thickening,
2		chlorate of soda,
2		sulphate of copper,
6		aniline salt.

Wheat Starch Thickening.

140	parts	wheat starch and
860		water are boiled together.

After cover printing, the goods are dried and steamed $^1/_2$ — 2 minutes in the Mather-Platt ager, then passed through the mixture of oxalic and sulphuric acids as previously described. After being thoroughly rinsed, the Aniline Black is developed by a passage through a soda solution at 100° F., containing 1 lb. soda ash per 10 gallons, and finally well washed.

3. The Chlorate Discharge.

a) General Remarks.

We preface our discussion of this process by a brief description of the prussiate discharge, for, although the latter now possesses no practical importance, it is of interest as the origin of the chlorate discharge in its present form.

In 1845* *Mercer* found that a mixture of red prussiate of potash (potassium ferricyanide) and alkali exercises an energetic destructive action on indigo without in any way injuring the vegetable fibre. Since a mixture of red prussiate and alkali decomposes too quickly for it to be used as a discharge by direct printing, *Mercer* first padded the material with the solution of prussiate, and then printed on thickened caustic soda. Owing to the high price of red prussiate, this method of working was very expensive, nevertheless, for lack of a better method the process was employed in this form for several years.

Lapis styles.

Later on the process was altered, and the thickened prussiate printed and dried, after which the goods were passed through warm caustic soda at 18° Tw. If alumina salts** are added to the printing paste, they are partially fixed by the treatment with alkali, and by subsequently dyeing with mordant dyestuffs coloured discharge effects (the so-called "Lapis styles") are produced.

---

* *Dépierre,* Traité de teint. et impress., vol. III, page 389.

** Compare *Sansone,* Zeugdruck, page 240.

With the discovery of the chromate discharge the prussiate method lost its technical importance and has only been retained here and there for special purposes. A number of proposals for its improvement were made, but none achieved practical success, and only the chlorate discharge, which arose out of it, acquired importance on the industrial scale.

First of all *Ch. Zürcher*[*] proposed to replace the caustic alkali by carbonates and bicarbonates. This process, however, made no headway, because the print was hygroscopic and ran during steaming.

This defect was avoided in the process of *C. Bloesch*[**] by using, instead of the alkali, carbonate or other salt of lead,[***] but this has the serious disadvantage that only pale grounds can be discharged.

A short time previous to this *A. Scheurer*[†] had published a paper on the same subject, in which he pointed out that certain insoluble ferricyanides, chiefly those of the divalent metals, *e. g.,* the magnesium salt, have a destructive action on indigo when steamed, even in the absence of alkali. Evidently *Bloesch's* process depends on the same reaction, and *Scheurer's* work was the inducement for its publication. *Scheurer* proposed at the same time as a further novelty a printing paste containing ferricyanide and acetates. The latter split up during steaming into acetic acid, which is given off as vapour, and alkalies or alkaline earths, which act together with the ferricyanide to discharge the indigo. As far as we are aware this process has not found practical application.

In his report on *Bloesch's* work *Jeanmaire* had already pointed out that the action of the red prussiate can be so much strengthened by the addition of chlorates to the printing paste that even dark grounds can be discharged, which is not the case with any of the processes above described. The technical application of this reaction was, however, prevented by the precipitation of iron and consequent soiling of the white.

---

[*] Bulletin de Mulhouse, February-March, 1876.

[**] Bulletin de Mulhouse, 1878, page 934.

[***] Report on the above process by *Jeanmaire,* Bulletin de Mulhouse, 1878, page 936.

[†] Bulletin de Mulhouse, 1878, page 157.

By the addition of chlorates the way was paved for the transition from the prussiate-caustic alkali to the chlorate discharge.

The firm of *Köchlin Frères* already referred to overcame the difficulty caused by precipitation of iron by their chlorate-prussiate discharge,* adding to the printing paste salts of non-volatile (chiefly organic) acids, which are readily dissociated on steaming. The recipe given by them only differs qualitatively from the usual chlorate discharge of to-day by the fact that, instead of the salts, the corresponding acids are directly employed.

Before this, *Persoz,*** *Schlumberger,**** and *Dépierre* † had mentioned the employment of chlorates (without addition of prussiate) for the discharge of indigo. *Persoz* prepared the material with chlorate of soda, and printed on a mixture of tartaric and hydrochloric acids, *Dépierre's* process depended on the destructive action of chromium chlorate on indigo when steamed, whilst *E. Schlumberger* found that aluminium chlorate will decolourise indigo.

Bromate Discharge.

Storck and *Pfeiffer* in 1884 drew attention to the fact that, when aluminium chlorate is the discharging agent, alumina can simultaneously be fixed on the fibre, and, by subsequently dyeing with Alizarine, red patterns may be produced. This process was further developed and made technically practicable by the observation of the favourable action of sodium bromide. *Brandt* †† prepared a discharge paste from aluminium chlorate, sodium bromide, copper sulphide, and potassium iodide, in which the decolourising action on indigo depended on the liberation of bromine on steaming, whilst the discharging property of the bromates was recognised by *Storck, Pfeiffer,* and *Binder,* ††† the first named pointing out the advantage of the bromates in being less injurious to the fibre than the chlorates.

Erban has recently published (Färber-Zeitung, 1905, page 337) his experiences of the use of sodium bromate in combination with bromide, the so-called "sodium bromide-bromate," and has given a practical recipe for this discharge. We may also refer to the exhaustive research of *Radkiewiez* on the chlorate discharge (Zeitschrift für Farben-Industrie, 1906, Nos. 23 and 24).

---

* Sealed note of 1889, opened 1899. Bulletin de Mulhouse, 1899, page 317.

** Traité de l'impression des tissus, part III, page 52.

*** Bulletin de la Soc. Ind. de Mulhouse, 1872, page 307.

† Bulletin de la Soc. Ind. de Rouen, 1877, page 52.

†† Bulletin de la Soc. Ind. de Mulhouse, 1892, page 201.

††† Bulletin de la Soc. Ind. de Mulhouse, 1892, pages 387 and 207.

In its present form, as usually carried out, the chlorate discharge consists in the combined action of a chlorate, or chlorate and bromate, and red prussiate of potash with a free or combined acid, the decomposing action of which takes place at a high temperature. The most suitable acids are non-volatile organic acids, such as tartaric and citric acids, but, since these acids act on the chlorate even when standing in the cold, they are only added to the printing paste just before use. When aluminium chlorate or bromate, which decompose more easily in steam, are employed, the addition of an acid-reacting substance is unnecessary; these alumina compounds are not at present used for white discharges, but only for the production of red on a blue ground by subsequent dyeing with Alizarine Red.

When the chlorate discharge has been employed, the discharged portions appear yellowish, from which it may be inferred that the indigo has been oxidised to a halogen derivative of isatine, and to obtain a pure white this must be removed by a treatment with weak alkali. We have seen that, in the case of the chromate discharge, there is a great danger of the fibre being tendered, and the discharging of large patterns or stripes is, therefore, to be avoided. With the chlorate discharge this disadvantage is absent, since there is nothing like the same tendency to the formation of oxycellulose as with chromic acid, and large designs can be produced without any fear of injury to the fibre.

The chlorate process is only suited for the production of white discharges, since the problem of finding colouring matters which remain unaffected by the chlorate and are fixed under the required conditions has not yet been solved.

The chlorate method will serve equally well for discharging the *R* and *G* brands of indigo.

It may be mentioned here that the *Fabriques de Produits chimiques de Thann et de Mulhouse* have brought into the market steam discharge pastes for indigo, with which good results can be obtained. Full details will be found in the pattern-cards and instructions issued by the above firm.

b) Instructions for the Chlorate Discharge.

White Discharge for Machine Printing.

First prepare the following

Standard Colours.

Standard *a*. Boil 150 parts starch with
1000 » water, and in the warm paste dissolve
430 » chlorate of soda by stirring.
Stir until cold and strain.

Standard *b*. Make 120 parts British gum into a paste with
200 » water, warm, and dissolve
340 » tartaric acid and
80 » citric acid in the paste.
Stir until cold and strain.

Both *a* and *b* are stable if kept separate, and these standards may be prepared for stock.

For printing make use of the following

Discharge Paste.

Mix 1100 parts Standard *a* with
300 » Standard *b*, and dissolve in the mixture cold
80 » potassium ferricyanide finely powdered. Carefully stir into the mass
100 » olive oil.

This discharge colour, being not permanently stable, should only be prepared in quantity sufficient for one day's requirements.

This recipe is intended for the discharge of dark grounds. For light shades it is suitably reduced in strength with the following

Starch Thickening.

Make 140 parts wheat starch into a paste with
860 » water, boil, stir until cold, and strain.

After printing, the material is dried and then steamed 3—5 minutes in the Mather-Platt ager at 212° F. in dry steam. The printed portions should appear yellow on leaving the steamer. If they are green, either the discharge is too weak or the length of steaming insufficient. Great care must be taken that the gaseous chlorine compounds evolved during the discharging process are rapidly removed by an ample current of steam in order that they may not attack the blue ground.

The goods are then passed through a

bath of silicate of soda

at $1\frac{1}{2}$—2° Tw. at a temperature of 195° F., and in this bath the discharged patterns become pure white.

Finally the material is washed in the usual way.

Pattern No. 12.

Chlorate discharge.

White Discharge for Block Printing.

Standard *a*. Boil together

250	parts	light roasted starch,
750	„	water, and
430	„	chlorate of soda, and add when cold
200	„	gum thickening 1 : 1.

Standard *b*. Boil together

120 parts British gum (powder),
200 » water,
340 » tartaric acid,
80 » citric acid, and stir until cold.

Before use mix together

1100 parts Standard *a* with
300 » Standard *b*, and dissolve in the mixture
80 » potassium ferricyanide, stirring in finally
100 » olive oil.

Otherwise proceed as described above.

Discharging Indigo with simultaneous Fixation of Alumina for the Production of Alizarine Red along with Indigo.

Discharge Paste.

120 parts (by weight) bromate of alumina 70° Tw.,
75 » » » thickening,
4·5 » » » magnesium carbonate.

The mixture is continuously stirred and heated for about $^1/_2$ hour on the water bath at 160° F. until it begins to show a faint yellow colour.

After printing, the goods are dried and steamed 5 minutes in the Mather-Platt ager, then passed through a bath containing

10 lbs. chalk and
3 » phosphate of soda

per 100 gallons water, well washed, and dyed with Alizarine. An addition of Turkey red oil (twice the weight of the Alizarine) is made to the dye-bath. Dyeing is commenced cold, the bath warmed in half an hour to 190° F. and kept for 1 hour at this temperature; the material is then washed, dried, steamed $^1/_2$ hour at 4 lbs. pressure, soaped, and finished.

The above discharge is for medium and dark blues, for pale shades of indigo it is suitably reduced.

VI.

Resist Printing.

1. The Process of Resisting by Mechanical Means.

a) Resisting by Tying, etc.

Resisting by Tying.

The oldest process for resisting the dyeing of indigo was probably carried out by tightly tying with threads the portions which were to remain undyed, or, where large surfaces were to be resisted, by wrapping with a protective layer of bast or similar material under the threads. These portions remained dry when immersed in the vat, and the deposition of colour was prevented; the resist was thus a purely mechanical one. This very old method, the so-called "bandana process," which can, of course, be applied to yarn as well as to cloth, was first carried out in the countries where indigo and indigo dyeing originated, *viz.,* India and the Indian archipelago, and is still extensively employed in those countries. Even among ourselves in Europe it occasionally re-appears as a new invention.*

Bandana Process.

It is easy to understand that in this way only comparatively crude patterns, such as spots and rings without sharp outlines, can be obtained. Fabrics of this kind are still produced in Europe to a limited extent for export.

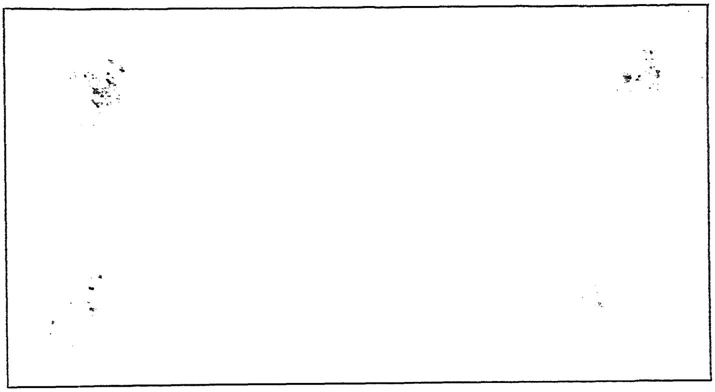
Chibori Method.

This form of producing designs has reached its highest development not in Europe, but in Japan, where it is widely used under the name of "Chibori." The tying up is there done partly by hand and partly by machines, and is applied both to uncut fabrics and to made-up garments. By alternations of large and small spots, rings, and patches, exceedingly tasteful patterns resembling rows of flowers can be produced even by this primitive method, and owing to the crape effect due to the tying of the fabric the design, when viewed from a short distance away, gives the impression of embroidery.

---

* See Zeitschrift für Farben- und Textil-Chemie, 1902, page 643.

Pattern No. 13.



Japanese Chibori style.

Resisting by Fastening the Material between engraved Boards.

A further development of this method of working consists in tightly fastening the material, either single or in several folds, between two boards provided with corresponding patterns. When the whole arrangement is immersed in the vat, the liquor finds its way between the engraved portions of the boards and dyes the material in those parts, but cannot penetrate to the portions under pressure, which correspond to the white pattern to be produced.

Compared with the method first described this mode of working, apart from the saving of labour, denotes a great advance, since the design is no longer confined to rings and patches, and the production of any desired figures in regular repetition is rendered possible, though the designs are still crude in form. This method also is employed in Japan, at any rate for yarn.

It is worthy of mention, because the simplest forms of hand blocks obviously originated from these boards bearing engraved patterns.

b) Battik Printing.

Wax Resists.

Another purely mechanical resist process also arose in the countries where indigo dyeing had its birth, and this process forms the transition to the usual European methods. We refer to the wax and resin resists discovered in India many centuries ago, and still carried out in the same form to-day, especially in Java on a very large scale under the name of Battiks.*

Battiks.

The usual garment of the native in these countries, the "sarong" and "slendang," consisting of a few square yards of cotton, is first painted with the negative of the picture or pattern desired by means of hot liquid wax or mixtures of wax or ceresine with resin. This is accomplished with the aid of the "tjantings," small copper cans provided with a handle and a narrow spout. Less important parts of the design, which recur frequently, are printed with copper stamps known as "tschaps." When the material is dyed in the vat, and the resist removed by boiling water, the positive of the design shows as a blue pattern on a white ground. Owing to a peculiarity of the wax resist, which it does not share with any other substance employed for the same purpose, a secondary effect is always produced by the Battik process, which was at first considered undesirable, but subsequently valued as a proof of genuineness. Since the resist on cooling becomes brittle, it is impossible to avoid cracking it when handling the material before and during the dyeing operation. The dyestuff will then find its way into the cracks, and the resisted portions will be thus irregularly covered with a fine network of coloured veins.

Formation of Veins with Wax Resists.

Combination of several Colours in Battik Printing.

As may be gathered from the above description, the Battik process not only permits of an unbounded freedom of design, but considerably widens the limits of colour production. Of course, the fabrics produced according to any of the processes previously described can be dyed again with any colouring matter which can be fixed without destroying the indigo ground, but in this way the white and blue design is only replaced by some other two-colour effect, in which the colour used for topping takes the place of the white, and the blue ground gives place to a mixture of blue with the topping colour. These limitations entirely disappear in the Battik process. If after removal of the first resist the blue and white fabric is again "battiked" and dyed with any colouring matter which can be fixed in the cold — this being the sole limitation, to which the method is subject — a two-colour effect including the blue is produced, if the second resist completely covers the first blue pattern. If the new resist only partly covers the old, then three or even four-coloured designs may be produced by suitable selection of patterns. This can be most clearly shown by an example. A favourite combination for sarongs consists of indigo with a brown similar in appearance and properties to catechu. If the second pattern exactly covers the first, a blue and brown design results, if the blue is not completely covered, blue, brown, and black (the latter from a combination of blue and brown) will be obtained, whilst, if the second resist covers a portion of the blue and a portion of the white, the design will be in blue, brown, white, and black. Even then the possibility of combinations produced by the Battik process is not exhausted, since by fixing a mordant by a cold process and, after removing the resist, dyeing warm with a mordant dyestuff, the colouring matter will only be fixed in the mordanted portions. We shall have occasion later on to recur to this method of working. It is evident from the above description that the production of colour and design depends almost exclusively on the skill and taste of the workman. If his talents rise to an artistic level, it is possible for him by an enormous expenditure of patient labour to produce fabrics, which, in the same way as the oriental carpets, take a high rank among the productions of industrial art.

---

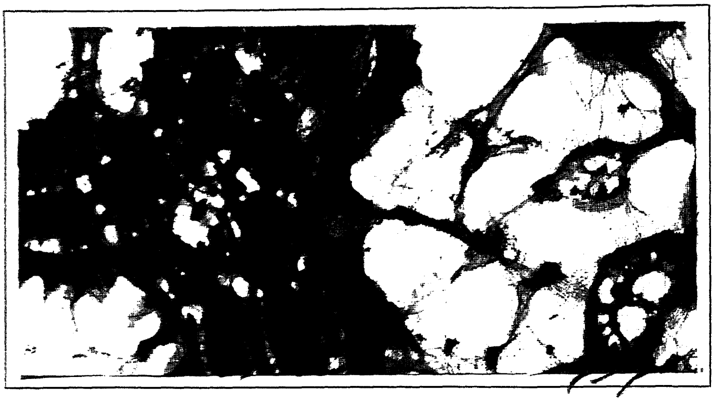
* An exhaustive description of this method is given by *G. P. Rouffaer* in his paper "Over Indische Battik-Kunst, voraal die op Java," which appeared in the Bulletin van het Kolonial-Museum te Haarlem, No. 23, and in his book "De Battik-Kunst in Nederlandisch Indie en har geschiednis" (Kleinmann, Haarlem). Compare also the communication "Über die Battiktechnik" by *W. Nieuwenkamp*, Textil- und Färberzeitung, 1903, No. 45.

Artistic Value of Battik Printing.

No one, who has had an opportunity of seeing the costly "battiked" sarongs with their bizarre designs and harmonious arrangements of colour, with which the wealthier native inhabitants of Java satisfy their cravings for luxury, will deny that these fabrics possess a high artistic value.

This possibility of artistic production has caused in Holland (by reason of its close relations with Java) efforts to be made to enlist this beautiful process in the service of modern artistic industry.*

Pattern No. 14.



Battik.

The above detailed discussion of the processes in use in the countries where indigo and indigo dyeing originated, processes, which cannot lay claim to being printing processes in the exact sense of the term, could hardly be justified in a survey of the application of indigo in printing unless a close connection with the subject could be shown. That such a connection exists, is proved by the facts that the first European prints were direct imitations of Indian styles, as is expressed in

Indian Print.

the now obsolete name of "Indian print" for any calico print, that the oldest resist processes in Europe depend on the application of wax, and that the Battik process, or at any rate wax resist processes, are at present carried out extensively in Holland and Switzerland for materials intended for export.

Battik Imitations for Export.

A direct adaption of the whole process, *i. e.,* painting with wax, to industrial production is rendered impossible by the great expenditure of hand labour involved, and the small output with such methods of working. Any imitation must, however, show the veins above described, and for the production of these the use of a wax resist is essential. The plan adopted has been to print on the wax resist. Printing with melted wax on mechanical printing machines is not possible, and the use of the process has thus been confined to block printing.

---

* Compare "Over de toopassing der Battik-Kunst in Nederland," by *H. A. Baanders,* Bulletin van het Kolonial-Museum te Haarlem, No. 23, and "Studiën in Battik-Techniek, onderzoekingen in het laboratorium van het Kolonial-Museum te Haarlem," by the same author.

Wax Resists on Silk.

The wax and resin resists, in addition to being used for these purposes, are employed in silk dyeing, since the other resist pastes used for cotton are unsuitable for this fibre. The silk is dyed in the vats in use for cotton, *viz.,* the copperas or zinc-lime vat, but with the addition of less chalk, and after dyeing the resist is removed either by soaping or by washing with benzene. This method is not of great importance, but it is carried out to a limited extent in England for goods to be exported.

c) The Application of Mechanical Resists by Stencilling.

Application of Starch Resists with Stencils.

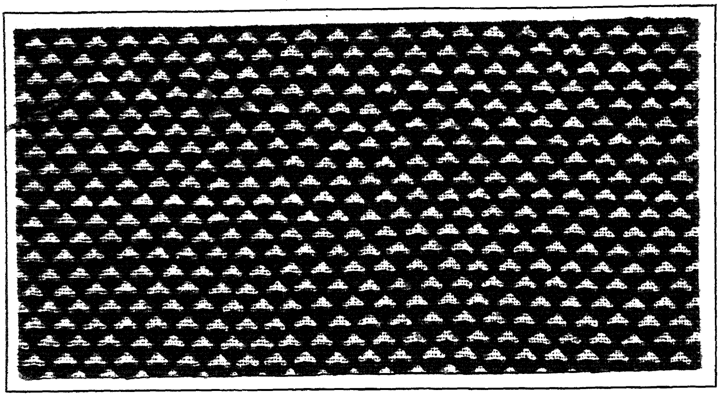
Before we leave the subject of the methods in use in Asia we must refer to the process of producing a resist by means of stencils, which has acquired a great importance in China, and even more so in Japan, and is to-day the chief method employed in these countries. The Japanese use for applying the resist not the hand blocks employed in Europe, bearing a raised pattern formed by wooden or brass pegs and bars, but special stencils made from a remarkably tough and strong paper, which does not become soft even on prolonged wetting, and is of so firm a texture that it allows of the formation of patterns with comparatively narrow connections of paper between the various openings.

White Patterns on Blue Ground.

With the aid of this stencil a paste of rice flour is applied to portions of the material by means of a thin, elastic piece of wood. This paste on drying has sufficient resistance to allow of dyeing in the vat even in dark shades.

Since, in all Japanese fabrics, the face and back of the cloth must be alike, the resist paste must be applied to both sides. In this way are produced white patterns on a blue ground.

Pattern No. 15.



Japanese stencil resist.

Blue Patterns on White Ground.

The problem how to produce isolated blue designs on a white ground without too great an expenditure of labour and material, such as would be necessary if large surfaces were to be covered with resist by the above method, has been very skillfully solved by the Japanese. In this case a stencil is employed which provides the portion of the material forming the blue design with a broad edge of resist paste. When the pattern has been applied for the first time, the material is folded over, and the second layer sticks perfectly fast to the fresh paste. On this layer of material the pattern is applied in exactly the same place, the fabric is again folded, when it again sticks together, and is stencilled once more, and so on, so that 40—50 layers of material adhere tightly together in the printed parts. The whole is then pressed together between two boards, which are cut out to correspond with the size of the pattern, the lower board being fitted with a pipe, and the upper one with a suction pipe. The vat liquor is drawn right through the whole pile of cloth, and in this way the same pattern is produced on both sides of every layer of cloth and in the portions desired. Patterns in several colours may be produced according to this process. The paste is easily removed from the material by washing.

This process, just as those previously described, requires a large amount of hand labour like our block printing. In spite of this these are, as already stated, the chief methods in use in

Japan, and it is astonishing what perfection of workmanship can be attained with this primitive apparatus. As a consequence of the strong artistic sense, which seems to penetrate the whole people, the Japanese designs far exceed from an artistic point of view the effects we produce by resist printing. They can without hesitation be placed on a level with the designs produced by the Battik process already described.

This short survey will suffice to show the stages of development of blue printing in the Asiatic home of indigo dyeing. No advance beyond the resist process has been made, and even those who have achieved the best results confine themselves, as has been pointed out, to purely mechanical methods of preventing the colouration of the fabric.

2. Resists, which act both chemically and mechanically. The "Blue Print."

a) General Remarks.

The fundamental difference between the most highly developed Asiatic methods and those in use in Europe* lies in the fact that in the latter the resist does not consist merely of a thickening, but without exception contains additions which strengthen the action of the resist, and may also allow of the production of coloured designs of a nature which cannot be produced by dyeing the resisted material.

The acid and oxidising Additions to the Resist.

The most important of these additions consist of salts, which act chemically upon the vat liquor by reason either of their acid or oxidising character.* In either case the colouring matter is precipitated in the printed parts in an insoluble state either as indigo white or as indigo before it can penetrate the resist. The fine layer of precipitated colouring matter, which covers all portions printed with the resist, forms in its turn an impervious layer, and thus strengthens the action of the resist.

---

* The best descriptions of blue printing are contained in the works of *J. Persoz,* "Traité théorique et pratique de l'impression des tissus" (Paris, V. Masson, 1846), and *J. Dépierre,* "Traité de la teinture et de l'impression" (Paris, Baudry & Cie., 1893). The brief but exceedingly lucid work of *M. Prud'homme,* "Teinture et Impression," is also worthy of mention.

This group of salts includes mercuric chloride (corrosive sublimate), copper salts, and a number of nitrates. Another group, to which zinc, aluminium, and soluble lead salts belong, occupies with respect to the action of the salt a middle position, since these salts act both as chemical and mechanical resists, the acid reacting as above described with the alkaline indigo solution, so that the hydroxide is precipitated in the resist in a gelatinous form, thus rendering the thickening still more insoluble and impermeable.

Of all these resisting agents, the copper salts, *viz.,* copper acetate and nitrate and verdigris, are by far the most important; the employment of all other salts has for the most part been given up or is restricted to special cases. Lastly must be mentioned those additions to the resist paste, which exercise a purely mechanical effect, *viz.,* China clay and lead sulphate. Their chief use, however, lies in another direction, they permit of the production in a special manner of coloured resists on a blue ground.

Coloured Resists.

If a paste containing lead sulphate is printed on cotton material, a portion of the salt, in spite of its insolubility, penetrates into the fibre, where it is tenaciously held. This absorption of lead sulphate by the fibre is so considerable that it is possible in this way, under the conditions of resist printing, to load the printed portions with lead compounds more easily than is possible by the use of soluble salts. A complete explanation of this fact has not yet been found. The lead sulphate, which is converted into basic sulphate by the action of the alkaline vat liquor, is so firmly fixed on the fibre that the greater part of it resists all the operations which follow printing, *viz.,* dyeing, souring, and washing. If a material thus treated is finally passed through a bichromate solution, yellow chromate of lead is formed on the printed portions, or, if a boiling alkaline solution of neutral chromate is employed, orange coloured basic chromate is formed, and this may be converted into a cream shade by afterwards passing through warm dilute oxalic acid.

---

* A very thorough treatment of this subject from the chemical standpoint, extending to the action of substances not yet technically employed for the purpose, will be found in *M. P. Schützenberger's* "Traité des matières colorantes" (Paris, V. Masson & Fils), vol. II, page 580. The chief portions of this excellent work, which appeared as long ago as 1867, cannot even yet be considered antiquated.

Reference may further be made to a more recent publication by *Tagliani* (Zeitschrift für Farben- und Textilindustrie, 1904, page 443, etc.).

If the resist is printed not on a white, but on a pale blue indigo ground, green and olive patterns are obtained in place of yellow and orange. It is thus possible by means of resist printing to produce white, pale blue, yellow, green, orange, olive, and cream coloured designs, and by suitably working and employing a resist paste free from lead and containing China clay alongside a paste containing lead it is possible to produce a great variety of combinations of two or more colours.

Lapis Style.

Red designs cannot, however, be produced directly by the resist method. To obtain this end, roundabout and complicated processes must be adopted, which add greatly to the difficulty and cost of production. The oldest process of this kind* makes use of the property of many aluminium salts of precipitating their base on exposure to air. If such salts are mixed with the resist paste, a portion of the alumina becomes fixed on the fibre either on drying or in the alkaline vat. This on subsequent dyeing with Alizarine serves as a mordant for the dyestuff, and only the resisted portions are dyed. Besides Alizarine other colouring matters, which can be fixed on an alumina mordant, can be similarly employed. This style, known as "Lapis," was at one time greatly esteemed for its beauty and fastness, it is, however, difficult and expensive to produce, and was abandoned many years ago.**

Azo Resists.

In recent times there is to be recorded only one attempt to solve the problem of the production of a fast red under vat blue in another way. This was by means of Paranitraniline Red.

---

* *Schützenberger,* "Traité des matières colorantes," vol. II, page 583.

** A large number of the most varied recipes for the Lapis style produced according to the resist method are to be found in the exhaustive treatise of *C. F. Kreyssig,* "Abhandlung über das Bedrucken, Bleichen und Färben der gewebten Zeuge" (Berlin, 1835, published by the author, 4 vol.).

*Donald** proposes to pad the material with beta naphthol, and then to print on a resist paste containing diazotized Paranitraniline or Nitrosamine and acid together with zinc salts, the latter being substituted for the corresponding copper salts. The process suffers from the defect that the printing colours very quickly decompose. *Lurati*** has suggested a similar process.

If Paranitraniline is replaced by other bases, other colour effects are produced, *e. g.*, a bright fast orange with Metanitraniline. By combinations with basic dyestuffs *Lurati* obtained coloured resists, but the process is rather complicated.

A very primitive expedient, which is actually made use of to a limited extent, is to print a red oil colour on the goods after dyeing, fitting it in to the resisted pattern (see page 116).

By the addition of Thiazine Red to the ordinary resist colour a bright, fast pink may be directly produced.***

Combination of Resist Printing with Aniline Black.

A favourite combination is that of indigo with black. Before the introduction of Aniline Black, a logwood black or iron black was employed.† Since these, however, are not sufficiently fixed when printed in a resist paste, the resist was dispensed with, and the black printed on the white ground. On subsequently dyeing in the vat the black design was not destroyed or covered, but rather intensified. In this way it was possible to produce black patterns on a blue ground, fitting in, if desired, an ordinary white or coloured resist, or by cover printing with the resist paste black patterns partly falling on the white could be obtained.

Aniline Black can be well fixed from any indigo resist, especially from those containing mercuric chloride, and since the introduction of this black it is possible without cover printing to obtain black designs leaving the other resisted patterns unaffected. For this process any Aniline Black is suitable which can be developed by hanging in the air. Cover printing with a steam Aniline Black is also possible, but not usual, since the production of these prints is for the most part carried out in small print works, which lack the necessary apparatus. Mention may also be made of the peculiar use of Aniline Black in connection with a resist process invented by *Cabiati,*[*] which consists in cover printing the resisted material with a network of Aniline Black and then dyeing in the vat. This process effects a saving of indigo and imparts to the fabric a velvet-like appearance.

---

* Dyer and Calico Printer, 1897, page 25.

** Austrian patent No. 8411 (expired).

*** This process is described by *H. A. Schumacher* in German patent No. 148 501 (expired).

† Compare *Kreyssig*, vol. II, page 508 et seq.

Prussian Blu Resist.

This completes the description of the processes depending exclusively on the principle of resisting, which have been or still are in general use in western Europe. In the Slavonic countries of eastern Europe certain other methods are carried out, of which we have but little knowledge. In these processes the pale blue, and thus also the green, olive, etc., are not produced by dyeing the goods a pale shade in the vat before printing the resist, but by means of Prussian blue. In the "blue print" works of these countries it is not usual to boil out the material before dyeing, the cloth being taken direct from the loom for dyeing and printing. This crude material is so difficult to wet out that it is not possible to dye the pale blue ground necessary for pale blue, green, etc., patterns sufficiently level. On the other hand, the crude cotton fibre has the property of fixing finely divided Prussian blue added to the resist paste in the same way that boiled out cotton fixes sulphate of lead, as already described. On cotton, which has been boiled out, the blue is fixed to a much smaller extent, insufficient for most practical purposes.[**] If the resist contains lead sulphate, in addition to the blue green and olive can readily be produced by a subsequent chrome bath. This method of employing Prussian blue certainly does not yield very fast prints — Prussian blue, as is well known, is destroyed by alkalies and is not so fast to light as indigo — but possesses the advantage of simplicity. By employing this process it is possible to produce besides white and coloured resists which require a white ground (yellow, orange, cream) also pale blue and resists containing blue (green, olive) by simultaneous printing without having to dye a ground of light blue in the vat.

Discharge Resists.

Another solution of the problem how to avoid the defects and difficulties of resist printing has been found in the use of discharge resists, which when printed on a pale blue ground destroy the indigo in the printed portions, so that on dyeing again in the vat, in spite of the pale blue ground, white patterns on a dark ground are produced. By simultaneously printing an ordinary resist paste along with the discharge resist, pale blue and white designs on a dark ground, and, by varying the method of working, coloured designs in white and green, etc., on a dark ground are directly obtained.

---

[*] German patent No. 90067 (expired).

[**] It is a remarkable fact that not all finely divided insoluble pigments are held in this way by the fibre, *e. g.,* all attempts to fix very finely divided iron oxide red in this way have proved fruitless.

The simplest of such processes consists in making use of the yellow and orange chromates, produced as already described, for discharging the pale indigo ground, since this necessitates no alteration in the resist. For, if the material printed with the yellow or orange resist is afterwards passed through an acid bath, a portion of the chromates is decomposed — the amount depending on the temperature — and the liberated chromic acid exercises a destructive action on the indigo.

This observation is very old, and the reaction has been made use of for a long time to brighten orange designs, which are dull owing to small amounts of precipitated indigo having penetrated in the vat through the resist to the cloth. *Kreyssig* described this "clearing" of yellow or orange resist prints in 1835, but, as far as can be learned from existing literature, the further step of directly discharging the pale blue ground was not taken. *Persoz* too was not aware of the method of discharge resists, and he solved the problem of the simple production of white along with pale blue in another way to be described later on.

As far as we know the earliest description of the employment of discharge resists along with ordinary protective resists is contained in the book "Färberei und Druckerei" by Dr. *W. H. Kurrer* and *K. Engels* (Leipzig 1874, G. Weigel), page 189. *E. Paul* has given several recipes for discharge resists in Dr. Lehne's Färberzeitung, 1889, page 255.

Discharging with coloured insoluble chromates produced on the fibre is employed at present chiefly in the production of cream along with pale blue, a very favourite combination. We shall give later on full instructions for producing this style.

b) Instructions for Resist Printing.

Preparation of the Material.

The material to be printed is generally lightly starched, which renders the printing easier and the dyeing better and more level; a thin paste of $^3/_4$—1 lb. starch per 10 gallons water is usually employed. If glue (1/2 lb. per 10 gallons) is also added to the starch, the brightness and reddish tone of the shade are increased, especially in light shades. Frequently the pieces are also calandered or mangled before printing, especially in two-sided printing, to prevent the resist from penetrating.* If dyeings of medium depth are to have a dull greenish shade or heavy dyeings a blackish blue appearance, the material may be prepared with copper salts as described on page 67. A considerable effect is produced even by an addition of 1/2 lb. copper sulphate to 100 gallons of the ordinary starch paste. In addition to the alteration of shade the cloth prepared with copper takes up the indigo more rapidly.

The resist paste may be printed either by means of hand blocks, with the perrotine, or with rollers, the most usual being the perrotine worked either mechanically or by hand.** Midway, as it were, between the perrotine and the roller machine is the printing machine with a roller provided with a raised pattern. A difference between block or perrotine printing and machine printing is that in the former methods the colour lies more on the surface, and they are, therefore, better suited for two-sided printing, whereas machine prints penetrate the fabric to a greater extent. This depends, of course, also on the consistency of the printing colour, with regard to which no rules of general application can be laid down. On the whole a thinner, smoother paste is required for hand or perrotine printing than for machine printing, and in the latter special care must be taken that any components of the printing paste not in solution are in an exceedingly fine state of division to prevent the colour from sticking in the engraving of the rollers. For machine printing deeply engraved rollers must be employed. The consistency of the paste can be regulated at will by varying the thickening agent, the addition of water, and the duration of heating. After printing, the material must be well dried, but not at too high a temperature, to thoroughly harden the paste; the longer the drying operation, the better will the resist hold in the vat.

Wetting out of the Resist printed Material.

After drying, the pieces are hung on a dipping frame and immersed in a wetting-out vat; this may be an old exhausted dye-vat or may be specially prepared with, for example, 30 lbs. quicklime, with or without 10 lbs. soda ash, per 1000 gallons of water. The object of the wetting-out vat is to avoid soiling the dye-vat by detached fragments of resist paste, and in addition to this a neutralisation of the acid salts in the resist takes place, and the metallic oxides are precipitated, whereby the paste is rendered harder and more resistant. The goods remain in the wetting-out vat for about 10 minutes, the frame being screwed up, so that the goods are tightly stretched and the folds are not in contact with one another.

---

* German patent No. 165 556 (1904).

** Perrotines for hand printing are supplied by *W. Vogel,* Reichenbach i. Schl., for machine printing by *C. G. Haubold jr.,* Chemnitz.

To effect a saving of indigo, when the goods are printed on one side only, the pieces are hung on the frame back to back.

Dyeing is carried out in the usual manner for the dipping vat; the zinc-lime vat is usually employed, occasionally the copperas vat. For the hydrosulphite vat the usual resist cannot be relied upon; a good paste may resist one or even several dips in a hydrosulphite vat, but there is always a risk that the resist may be loosened in places. For the hydrosulphite vat a special treatment of the resist is necessary, which will be described in a subsequent chapter (page 221). In order to avoid removal of the resist the dips must not last more than 15 minutes, and after each dip the position of the frame is reversed for the sake of level dyeing. As in the case of plain shades, dyeing is commenced in weak vats and continued in stronger and stronger vats, and for dark coppery shades dyeing is finished in a concentrated vat. The number of dips varies according to the shade; for a very deep blue even 12—15 dips may be given. The resist paste is washed off after dyeing in the manner given below for each different case. It is advantageous to dry the dyed pieces before removing the resist or treating further, the depth of colour being considerably increased in this way.

Finishing of Resist printed Goods.

Where, as is often the case, a very blackish tone is desired, this is obtained in the finishing process. A method yielding very deep shades is as follows:

The goods are twice starched at 120° F. in a size of 2 lbs. starch per 10 gallons, to which an addition of fat (tallow, lard) is made. After the first starching they are dried, but not too hard. Finally they are calandered. Dextrine and glue give less blackish shades.

A single treatment in a mixture of

½ lb.	starch,	per 10 gallons
5 oz.	fat (tallow, etc.)	

at 140° F. suffices to alter the shade considerably towards blackish brown. This leaves the goods quite as soft as if they had not been finished.

We now proceed to the description of the various printing processes.

Production of White and Pale Blue Designs.

White and Pale Blue Designs.

For white and pale blue, the latter on previously dyed material, resists may be employed which do or do not contain lead, but naturally only the latter when yellow or orange are to appear along with the white. A great number of tried recipes has been published, but it is not possible to mention any definite proportions as the best under all conditions.

For perrotine and block printing the following resists are suitable:

1. White Resist free from Lead.

30	parts	China clay,	
30	»	water,	
10	»	copper sulphate	in finely powdered state,
5	»	copper nitrate	
35	»	gum solution 1:1.	

The whole is heated on the water bath and made up to 100—110 parts.

2. Resist containing lead, for White and Yellow.

20	parts	China clay,	
20	»	water,	
10	»	copper sulphate	in fine powder,
10	»	lead nitrate	
20	»	lead sulphate in paste (about 60%),	
20	»	gum solution 1:1.	

The lead sulphate paste is prepared by mixing the hot solutions of 38 parts lead acetate and 33 parts Glauber's salt crystals (or 15 parts calcined sodium sulphate). The precipitate, which rapidly settles, is washed several times by decantation, and the mass allowed to drain on a filter to a stiff paste, which will contain about 60 % sulphate.

3. White Resist containing Lead.

25	parts	China clay made into a smooth paste with water,	
8	»	copper sulphate	finely powdered,
8	»	lead nitrate	
8	»	lead acetate	
$^{1}/_{4}$—$^{1}/_{2}$	»	fat or oil,	
14	»	gum solution 1:1,	
12—18	»	water.	

4. Resist for White and Yellow.

6	parts	China clay,
3	»	verdigris,
2	»	alum,
2	»	copper sulphate,
5	»	lead nitrate,
4	»	lead acetate,
$2^{1}/_{2}$	»	gum solution 1:1.

The China clay, verdigris, and gum in the state of fine powder are allowed to soak separately in water for several days, adding a little vinegar in the case of the verdigris; the alum and copper sulphate are prepared in hot concentrated solutions. The first three are carefully kneaded together, the alum and copper sulphate added, the whole heated to boiling, lead nitrate and then lead acetate added, and the mixture after stirring until cold is passed through a sieve. Water is then added until the required consistency is reached.

5. White Resist with Gum Substitute.

25	parts	water,
11·5	»	copper sulphate,
3	»	lead acetate.

When dissolved, made up to 45 parts.

30	parts	of the above solution,
8	»	wheat flour,
2	»	British gum,
2	»	calcium acetate solution 9° Tw.,
1	»	olive oil.

The mass is boiled and water added as required.

The use of thickening agents other than gum is not to be recommended.

For machine printing we recommend the following:

Resist free from lead I (for Machine Printing).

140	parts	light roasted starch are made into a paste with	
350	»	water, the paste stirred with	
150	»	gum solution 1:1, and in this mixture	
150	»	copper nitrate 90° Tw.	are dissolved warm, and the whole well stirred.
150	»	copper sulphate in fine powder	
50	»	copper acetate 90° Tw.	
		After cooling	
10	»	oil are mixed in evenly by thorough stirring.	
1000	parts.		

Pattern No. 16.

White resist.

Resist containing Lead II (for Machine Printing).

110	parts	light roasted starch,
275	»	water,
135	»	copper sulphate,
110	»	lead nitrate,
215	»	lead sulphate 60 % paste,
55	»	lead acetate,
10	»	oil,
90	»	gum.
1000	parts.	

Made up like I, except that the gum solution is stirred last of all into the mass after cooling.

Treatment of the White Resist after Dyeing.

To obtain white designs, the resist is removed after dyeing by warm souring. The pieces are passed through two baths, both at 105° F., the first containing 2 lbs., the second 1 lb. of sulphuric acid 168° Tw. per 10 gallons of water. The acid liquors are contained in wooden becks lined with lead, and the cloth passes over wooden rollers. Immediately after the acid treatment the goods are thoroughly rinsed, and the indigo removed in souring and washing is recovered as described on page 102.

Re-dyeing of White resisted Material.

In certain districts (Saxony, Pomerania) the goods printed with a white resist are dyed again with Alizarine Red or with brown dyestuffs, such as Kryogene Brown or Oxamine Brown, whereby red designs on a black ground or pale brown patterns on a brownish black or black ground are obtained.

Production of Yellow, Orange, Green and Olive Designs.

Yellow Resists.

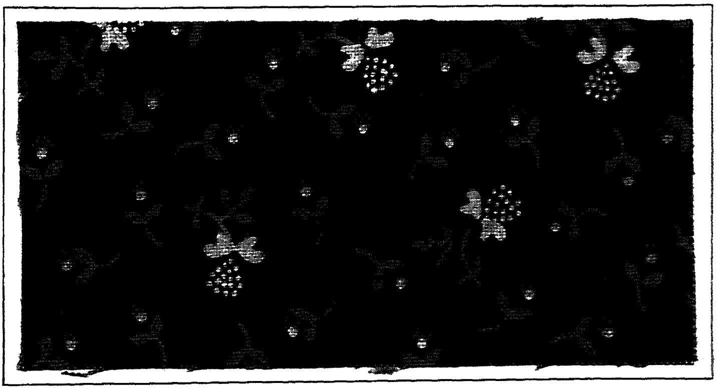
Yellow is produced by the formation of lead chromate on the fibre, the paste containing lead being after-treated with bichromate. The method of working is as follows:

The material is printed with one of the resists containing lead described above, dyed, soured, and rinsed as for white resists. It is then passed through a clear lime solution containing 1 lb. quicklime per 100 gallons, the vessel being automatically replenished from a reservoir. This is followed by rinsing, and the goods then enter a chrome bath containing 2 lbs. sodium bichromate per 100 gallons, where they remain for 20—30 minutes at 90—100° F. If it is desired to shorten the treatment, the amount of chrome may be increased to 10—12 lbs. per 100 gallons. Finally the cloth is thoroughly washed.

For the production of a fiery golden yellow the goods after dyeing pass directly into a bath containing 5 lbs. bichromate of soda per 100 gallons, where they remain for several hours at about 105° F., they are then rinsed, soured cold with 4 lbs. hydrochloric acid per 100 gallons, and well washed. The prolonged treatment in the chrome bath is requisite for the production of an intense yellow.

If the yellow obtained in the usual way is too greenish, it may be converted into a full golden yellow by treating for a few minutes at 120° F. in a soda bath containing 1/4—1/2 lb. soda ash per 100 gallons water. The concentration of the bath must be kept constant by replenishing with soda. The strength of the bath and the temperature must be exactly maintained, since a stronger action transforms the yellow into orange, nor is it advisable to use lime instead of soda, since the former tends to act irregularly and to produce too orange a shade.

Pattern No. 17.



Coloured resist.

Green is produced by printing a resist containing lead on material previously dyed a pale blue, and afterwards chroming in the manner described above.

Orange Resist.

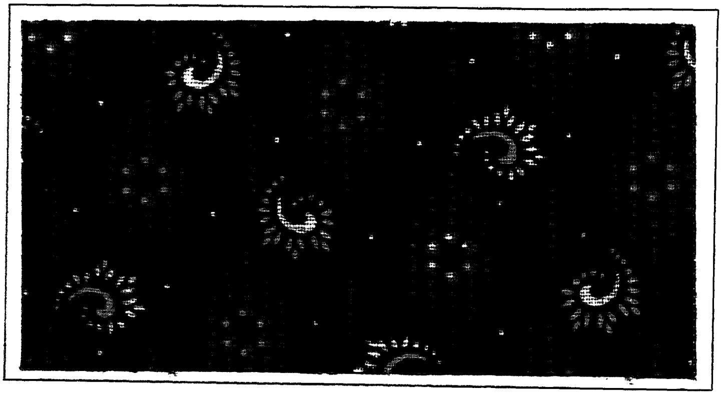
Orange is produced by the formation of a basic lead chromate on the fibre. The material is printed with the following

Orange Resist.

80 parts China clay } are ground together to an
100 » water } even paste, and
120 » copper sulphate } in fine powder are dis-
120 » lead nitrate } solved warm in the paste,
100 » lead acetate } which is then mixed with
250 » lead sulphate paste, thickened with
100 » gum thickening 1:1. Finally
10 » rape oil are added.

The whole is then heated with constant stirring, stirred until cold, and strained.

Pattern No. 18.



Orange resist along with white, olive, and pale blue.

For a brilliant reddish orange the following resist may be recommended:

16 parts British gum 1:1,
20 » water,
18 » copper sulphate,
24 » lead nitrate,
50 » lead sulphate 60 %,
18 » lead acetate,
9 » lead oxide,
25 » gum thickening 1:1.

By adding 3—5 % Cotton Red 4B extra to the resist a much redder shade is obtained.

After dyeing, the resist is removed with acid, as in the case of the white resist, and the material well washed in order that no acid may be carried over into the orange bath. This is prepared by boiling together 1 lb. bichromate and 4 lbs. quicklime per 10 gallons water, allowing to settle, and drawing off the clear liquor. The bath is contained in a vat provided with rollers (open-width continuous vat), through which the pieces are passed at the boil in $^1/_2$—1 minute. If they remain longer in the chrome bath the blue ground is injuriously affected, and after coming from the bath the goods should be washed at once. For replenishing the bath it is well to place a reservoir containing the bichromate-lime bath above the orange vat.

Olive Resist.

Olive is obtained by printing the resist containing lead on a pale blue ground, and then proceeding as for orange.

According to the processes already described the following combinations may be obtained:

1 **White - Light Blue - Dark Blue**	2 **White - Green - Dark Blue**	3 **White - Olive - Dark Blue**	4 **White - Yellow - Dark Blue**
Resist with or without lead on undyed cloth, dye pale blue, fit in same resist, dye dark blue.	Resist without lead on undyed cloth, dye pale blue, fit in resist containing lead, dye dark blue, and chrome.	Produced like No. 2, using orange resist and orange bath instead of chroming.	Two resists, with and without lead, on undyed material, chrome for the yellow.
5 **White - Orange - Dark Blue**	6 **Pale Blue - Olive - Dark Blue**	7 **Pale Blue - Yellow - Dark Blue**	8 **Yellow - Green - Dark Blue**
As No. 4, using orange resist and orange bath instead of chroming.	Print on material dyed pale blue a resist without lead and an orange resist, and pass through orange bath.	Print a resist containing lead on undyed material and dye pale blue. Fit in a resist free from lead, dye a dark blue, and chrome.	Print resist containing lead on undyed cloth, dye pale blue, fit in the same resist, dye dark blue, and chrome.

To ascertain, whether colours on the fibre have been produced by the resist process, it suffices to place the material in warm dilute hydrochloric acid, when yellow will become white, orange first yellow then white, green turns to pale blue, and olive first green and then pale blue. In the last two cases the acid must not be too strong or the chromic acid formed from the lead chromate will discharge the pale indigo ground to white. The proper concentration of the acid (about 1 part ordinary hydrochloric acid with 5 parts water at 105° F.) is soon ascertained by a few experiments.

Pale Blue and White on Dark Blue by means of Discharge Resists.

1. For Perrotine Printing.

Discharge Resist.

The pale blue dyed material is printed with a resist free from lead (*e. g.*, No. 1, page 205), and for white with the following discharge resist:

I	10	parts	China clay are mixed with
	35	»	copper nitrate 90—105° Tw.,
	3	»	wheat starch are stirred with
	10	»	water.

Also

II	15	parts	water,
	3	»	soda ash,
	9	»	sodium bichromate,
	18	»	zinc sulphate

are heated together. After cooling, I and II are stirred together until the mass has an even consistency.

2. For Machine Printing.

Resist for pale blue.

15	parts	light roasted starch,
36	»	water,
17	»	copper sulphate,
17	»	copper acetate,
15	»	gum thickening 1:1.

Discharge resist for white.

15 parts British gum in powder,
50 » water,
4 » soda ash,
12 » sodium bichromate,
24 » zinc sulphate

are boiled up together, and while still warm

20 parts copper nitrate,
20 » copper sulphate,
10 » gum thickening 1:1

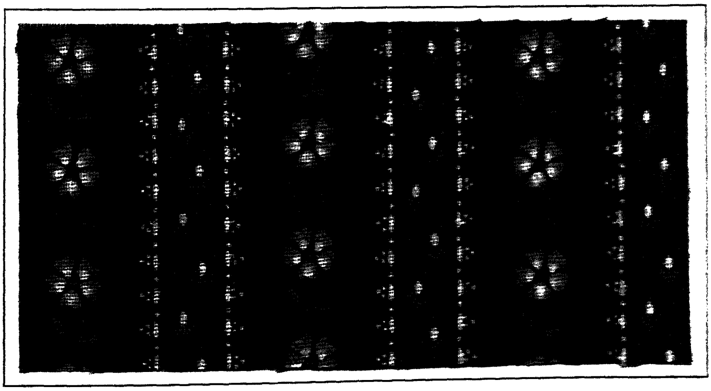
are added.

The printed pieces are well dried and dyed dark blue, then rinsed and passed through a cutting bath containing

7 lbs. sulphuric acid 168° Tw. } per 100 gallons.
7 » oxalic acid }

They should be passed through this bath as rapidly as possible ($^1/_2$—1 minute) to avoid any tendering of the fibre. The temperature is regulated so, that in a passage of this length a pure white is obtained, as a rule 120° F. is high enough. In any case the effect desired must not be brought about by prolonging the duration of the passage, but, if necessary, by raising the temperature of the bath. After the cutting bath the goods are well washed in running water.

Pattern No. 19.



Discharge resist.

Pale Blue, White and Yellow on Dark Blue by means of Discharge Resists.

The material dyed pale blue is printed with a resist containing no lead; a discharge resist for white also free from lead, as described in the last process, is then fitted in, and in addition the following lead discharge resist for yellow:

2 parts soda ash and
6 » sodium bichromate are dissolved in
10 » water, and
12 » zinc sulphate added.

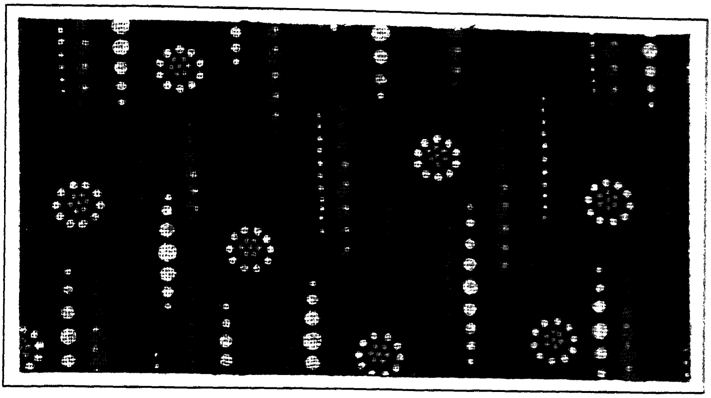
The whole is heated to 120° F. and well stirred. After cooling, 70 parts of the lead resist paste (2) given on page 205 are added.

The material printed with the three resists is dried and dyed dark blue, and, just as in the process last described, it is rinsed, passed through the cutting bath, rinsed again, and taken through a chrome bath to develop the yellow. This bath contains $^1/_2$ lb. bichromate of soda per 10 gallons, the pieces remain in it for 20—30 minutes at 95—105° F., and are finally rinsed.

Pale Blue and Cream by means of Discharge Resists.

The material is dyed pale blue, printed with one resist containing lead and one without lead, dried, and dyed dark blue. It is then soured as given on page 208 for a white resist, rinsed, and treated as given for orange on page 210. After the development of the orange, it is rinsed, quickly passed through a lukewarm (90° F.) oxalic acid solution at 3° Tw., and immediately thoroughly washed. The oxalic acid transforms the orange into Cream. cream and at the same time acts with the chromate to discharge the pale blue ground underneath.

Pattern No. 20.



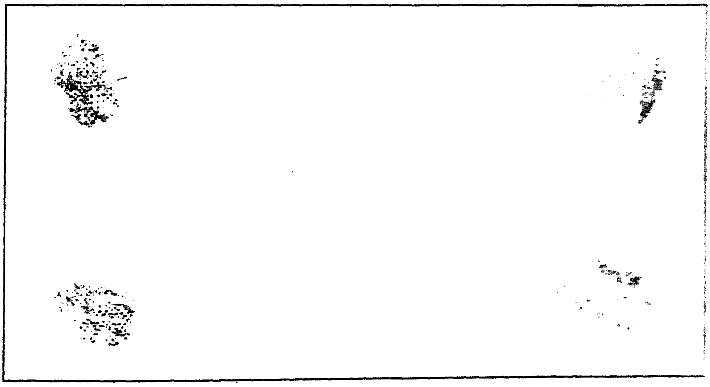
Discharge resist.

Pale Blue and Green with Prussian Blue Resist.

Prussian Blue Resist.

The undyed, starched material is printed with a resist containing no lead (*e. g.*, No. 1, page 205) and also with a lead resist (No. 2, page 205), to each of which 20—25 % Prussian Blue in paste has been added. After printing and drying, the pieces are dyed and then treated with acid and chromed as for the yellow resist.

Pattern No. 21.



Prussian Blue resist.

The fastness of this blue and green are, of course, not equal to that of the colours obtained by printing an ordinary and a lead resist on previously dyed material. By repeated washing in alkaline solutions the blue is changed to white and the green to yellow.

Red and Orange Resists with Azo Colours produced on the Fibre.

Red and Orange Resist with Azo Colours.

For red designs the well boiled-out material is starched with the following solution before printing:

10 parts starch are boiled in
490 » water, and when lukewarm
45 » Turkey red oil F,
15 » beta naphthol dissolved in
15 » caustic soda 70° Tw., and
425 » water are added.

The pieces prepared in this way must be dried at a moderate temperature (95—105° F.), and must not be allowed to lie too long, or they will become brown and give dull shades.

The red resist is thus prepared:

Stock resist.

200	parts	China clay,
200	»	water,
50	»	zinc acetate,
100	»	lead nitrate,
200	»	lead sulphate paste 60 %,
50	»	lead acetate,
240	»	gum solution 1:1.

Immediately before printing, to every 900 parts of the above stock resist are added cold 100 parts of the following solution, and the whole carefully mixed by stirring.

42 parts Nitrosamine Red are diluted with
50 » cold water, and
20 » hydrochloric acid 32° Tw. then added.
(Before use the solution is allowed to stand for 15 minutes.)

This solution must be kept in a cool place, and no greater quantity than can be used in half a day should be prepared at one time.

Instead of Nitrosamine the following Paranitraniline solution may be employed:

6·9 parts Paranitraniline are dissolved in
17·5 » hot water and
17·5 » hydrochloric acid 32° Tw., and after cooling diazotised by adding
54·3 » ice and
3·8 » sodium nitrite.

A red of a yellower tone and great brilliancy is obtained by using a solution of Chloranisidine prepared as follows:

7·8 parts Chloranisidine P (hydrochloride) are dissolved in
60 » hot water and
6 » hydrochloric acid 32° Tw., and after cooling diazotised by adding
23·4 » ice and
2·8 » sodium nitrite.

Pattern No. 22.

Nitrosamine resist.

After printing the resist, the pieces are hung in air for several days, then dyed in the ordinary manner, and the resist removed by souring at 85—95° F.

If a white design is required along with the red, a white resist is also printed.

In the case of orange the intensity and the yellowness of tone depends upon the amount of the diazotised base.

The process is as follows:

The boiled-out goods are padded with the following solution:

I	10	parts	wheat starch are boiled with
	500	»	water, then cooled and mixed with
II	8	parts	beta naphthol,
	8	»	caustic soda 70° Tw.,
	450	»	water,
	15	»	Turkey red oil F.

The padded material, as in the previous case, must be dried at a moderate temperature (95° F.) and must not lie too long. It is printed with the following

Orange Resist.

Stock resist.

200	parts	China clay,
200	»	water,
50	»	zinc sulphate,
100	»	lead nitrate,
200	»	lead sulphate paste 60%,
50	»	lead acetate,
200	»	gum solution 1:1.

To 950 parts of this stock resist 50 parts of the following diazo solution are added.

55	parts	Metanitraniline R are dissolved in
400	»	water and
85	»	(by volume) hydrochloric acid 32° Tw.,

and after cooling down completely

200	parts	ice and
30	»	sodium nitrite dissolved in
230	»	water are added.

The diazotised base decomposes very rapidly, and the resist should be printed as soon as possible.

The pieces are hung in air, dyed, and soured as in the case of the red resist.

Pattern No. 23.

Orange resist with Metanitraniline R.

Pink Resist with Thiazine Red R.

Pink Resist.

According to all experience up to the present Thiazine Red is the only dyestuff which, when added to the resist paste, becomes fixed in a fairly fast condition upon the fibre. The disadvantage of the process is the large amount of colouring matter required; according to the shade 10-15 °/o Thiazine Red R must be added to the resist. The best result is obtained by using resist No. 1, page 205, to which the dyestuff dissolved in hot water is added.

White Resist for Indigo with Aniline Black Cover.

White Resist for Indigo and Aniline Black.

The ordinary protective resists containing lead do not only resist indigo, but also Aniline Black, and this very completely if the resist paste is dry enough. The style is produced by printing a material prepared as usual for resist printing with a resist of suitable composition, drying well, and cover printing with an Aniline Black printing colour. The black is developed by hanging in a warm, moist atmosphere. The further treatment, dyeing, souring, etc., is just the same as usually employed for resist prints.

To resist the blue and black any good resist paste can be employed; we give a recipe below, which we have found to serve the purpose well.

Lead resist for indigo and Aniline Black.

15 parts	China clay,
25 »	water,
10 »	verdigris,
5 »	copper sulphate,
10 »	lead nitrate,
15 »	lead acetate,
20 »	gum solution 1:1.
100 parts.	

Pattern No. 24.

Resist for indigo and Aniline Black.

A simple Aniline Black for developing by oxidation in air is prepared from

100 parts	wheat starch thickening	dissolved in the cold.
6 »	Aniline salt	
2 »	potassium chlorate	
2 »	copper sulphate	

Wheat starch thickening.

120 parts	wheat starch	boiled 10 minutes and stirred until cold.
880 »	water	

Only sufficient colour for one day's use must be prepared at one time, since it decomposes if kept longer.

Resist Process for Continuous Vats (Zinc-lime or Hydrosulphite Vats).

(Process patented by *Franz Schaab* of Trier,
German patent No. 144286.*

Resist Process for Continuous Vats.

The ordinary resists already described have a sufficient protective action in the zinc-lime or copperas dipping vat, but cannot be used for the continuous vat, because the resist is partially or wholly removed by the friction caused by the pieces passing over the guiding rollers.** With the aid of *Schaab's* process mentioned above it is now possible to make the paste adhere so firmly to the fibre that it resists not only the mechanical friction in the continuous vat, but also the chemically solvent action of hydrosulphite. The process consists in printing the goods in the usual way with a suitable resist, and then padding with solutions of caustic alkali (caustic soda) or alkaline carbonates. On drying a hardening of the paste takes place, which is due to the action of the alkali.

Caustic soda is most suitable for padding, and the resists containing lead (*e. g.*, No. 2, page 205) are to be preferred.

The concentration of the caustic liquor may vary; by using caustic at 50—70° Tw. the padded side is dyed considerably deeper in the vat than the back; if the caustic is at 23° Tw., which suffices for the purpose, the two sides are dyed about equally. To the padding liquor is added about $^{1}/_{20}$ of its weight of dextrine or British gum. After drying, the pieces must be dried as warm as possible (115° F.) and for a considerable time. This thorough drying is important, since the complete hardening and thorough adherence of the paste depend upon it.

The favourable action of the caustic soda is not only exercised upon the resist, but also on the starch size usually employed before printing. Without this treatment the starch swells up in the alkaline vat and soils the rollers, so that the portions of the material coming after are stained, whereas the cloth padded with caustic soda is free from this defect.

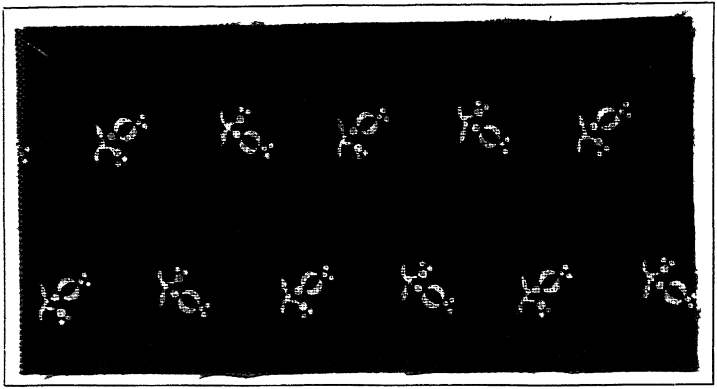
---

* Austrian patent No. 15707 of the Badische Anilin- & Soda-Fabrik.

** German patent No. 68823 describes the construction of a continuous vat, which permits of dyeing resisted material, but we have no practical experience of this process.

After dyeing in the continuous vat, the paste is removed as usual by washing with acids.

Pattern No. 25.



Resist style dyed in the continuous vat.

Part III.

The Application

of

Indigo pure B.A.S.F.

in

Wool Dyeing.

1. General Remarks.

General Remarks.

Of all blue dyestuffs for wool indigo has been from the earliest times the most important. It owes its extended application to its excellent fastness, which surpasses that of any other blue dye.

Indigo plays the chief part in the manufacture of military cloths; in all countries uniforms are dyed chiefly with indigo, either as a self blue or in admixture with white or black. In addition indigo is extensively employed in the preparation of dress goods, blankets, etc., and is used partly as a self colour, but still more as a bottom or in combination with other dyes for fashionable shades.

Owing to its purity, uniformity and cheapness, the synthetic product has almost entirely supplanted natural indigo in wool dyeing. Indigo pure is supplied ready for use and in such forms as are best adapted for the various vats and conditions of trade. The working of the vat no longer depends upon chance, as is the case with natural indigo, the methods of wool dyeing having been simplified and rationalised by the introduction of the synthetic article. Especially has the hydrosulphite vat been perfected owing to the success of the *Badische Anilin- & Soda-Fabrik* in producing a stable hydrosulphite of regular action, and this vat is gradually replacing the fermentation vat.

Wool is dyed with indigo in almost any stage of its manufacture, chiefly in the loose form, but also in the piece, as slubbing, and as yarn. Yarn is also occasionally dyed on bobbins.

The fastness and beauty of indigo dyeings on wool are almost entirely dependent on the condition of the vat, the method of working, and the purity of the wool. As has been previously explained, only that dyestuff is of value, which is actually fixed on the fibre, and in order that this fixation may be effected to the greatest possible degree it is necessary that the wool be completely degreased, that the vat contains no unreduced indigo, and that such dyestuff as is unavoidably loosely fixed should be removed by thorough washing.

It is obvious that a bright sky or medium blue can only be obtained on a white wool, and that the tone of a mixture consisting of blended blue and white will be dulled by the use in the blend of a yellowish wool.

In dyeing loose wool it has also to be remembered that during the subsequent processes of carbonisation and decatising, to which it will be subjected, an alteration of the shade towards red occurs, which alteration can be further increased by steaming. This has to be allowed for in dyeing to pattern, and still more must allowance be made with regard to depth of shade. Even with well dyed material there is always a loss of depth during milling and washing. For this reason the dyeing should be compared with the pattern only after well soaping or, if loose wool, after preparing a "felt pattern."

In the setting and working both of the fermentation and hydrosulphite vats particular attention must be paid to the quantity of alkali present. Excess of alkali injures the wool, while too little deleteriously affects the dyeing, hence the correct mean must be adhered to. Even a small excess of alkali over and above that necessary to keep the indigo white in solution, but which is yet not sufficient to act on the wool, may have a bad effect by retaining the indigo white in the vat and preventing or making difficult the production of dark shades. This action of the alkali may also lead to errors in estimating the strength of an indigo vat. In making comparative tests, it is, therefore, necessary to keep the amount of alkali in the various vats absolutely equal. The retarding influence of strong alkali may be illustrated by the fact that $^1/_2$ gallon caustic soda 42° Tw. added to a hydrosulphite vat of 1000 gallons causes a loss in depth of shade of about one-third. In the case of the fermentation vat there is less danger from an excess of alkali, because the process of fermentation can only be kept up in the presence of a certain degree of alkalinity, and the vat becomes abnormal in appearance as soon as the proper limit is exceeded. On the other hand, the amount of alkali in a hydrosulphite vat cannot be estimated with certainty from its appearance, and for testing this methods to be later described (pages 254 and 256) must be employed.

If a vat is worked with too little alkali, or should through any cause, *e.g.*, through the repeated dyeing of white wool or of carbonised wool, which has been insufficiently neutralised, too much alkali be withdrawn, the reduced indigo is taken up too quickly and gives rise to imperfect penetration, especially in the case of piece-goods.

In determining the amount of dyestuff necessary to produce a certain shade, or the comparative strengths of various brands of indigo, the influence on the depth of shade of the quality of the wool must not be neglected. A fine wool requires much more dyestuff than a coarse one, and in dark shades the difference may even be 15 % or more. In all comparative experiments with different varieties of indigo, or with different kinds of vat, it is necessary that the same quality of wool be used throughout.

In wool dyeing two kinds of vat are used, which widely differ in their character and in the manner in which the indigo is brought into solution, *viz.,* the fermentation vat and the hydrosulphite vat. In the former, solution of the indigo takes place in the dye vat itself, and is effected by what, to commence with, is a physiological process, whilst in the latter purely chemical reactions are brought into play, and the indigo may be, and usually is, dissolved in a vessel other than the dye vat.

2. The Fermentation Vat.

General Remarks.

Development of the Fermentation Vat.

The fermentation vat is the oldest kind of vat, and probably the oldest known dyeing process. The habitat of the indigo plant may be regarded as the country of its origin, from whence it has gradually spread over the whole world. Various forms of it are now extensively used.

The method of working the vat, as originally carried out, will, it is thought, have been much the same as that generally employed at the present day in oriental and Asiatic countries. It consists in the solution of the indigo by means of starchy and sacchariferous products (dates, raisins, the leaves of the henna plant, etc.) or parts of the indigo plant itself, in conjunction with vegetable ash, lime, or soda. In this vat, which is usually set and worked cold, silk and wool may be dyed fast and beautiful shades. This fact is worthy of note, as the impression is common that wool cannot be dyed in a cold vat. For the European dyeing industry, however, the above method is useless, because it is too slow and cumbersome, and is not sufficiently productive.

In a recipe from the year 1431 honey is proposed as a fermenting agent, and the honey vat is to this day used in the Caucasus for dyeing carpet yarns.

The precursor in Europe of the modern fermentation vat was the woad vat, set with the indigotic leaves of the woad plant (isatis tinctoria), a member of a different genus from that of the indigo plant (indigofera). It is still cultivated,* as the woad obtained from it is a valuable fermentative agent. The woad vat itself originated through local laws making it compulsory for indigo to be worked together with woad, and a similar form of vat is still occasionally used.

Towards the middle of the forties the setting and working of the fermentation vat was greatly improved through the employment of sugar syrup, which was first recommended by the dyer *B. Neumann.* The working was thus simplified and made comparatively certain, so that the old vat recipes were generally abandoned.

The processes, to which the reduction of indigo in the fermentation vat is to be attributed, are not yet clearly understood. The conversion of the indigo into soluble and tinctorially active indigo white is due to nascent hydrogen, which is generated from sacchariferous and starchy products by means of a fermentation process. Lactic, butyric, acetic, and carbonic acids are likewise formed, but, so far, no organic reducing agents have been isolated. This fermentative process is set up by microorganisms,** among which, according to recent researches of *Wendelstadt* and *Binz,**** are to be found species both of bacteria and yeasts. They have the common peculiarity of dying when kept for some time at a temperature of 180° F. or over. They occur in bran, flour, madder, and wood, and owe their presence in natural indigo to its method of preparation.

---

* Chem. Zeitung, 1904, page 1229.

** *Fritz,* Berliner Berichte 11, page 1890.

*** Berliner Berichte, 1906, page 1627.

Attempts have been made* to put the working of the vat on a better footing and render it less empirical by the employment of pure bacteria cultures, but successful practical results have not been obtained. It hardly seems likely that a simplification of the process is to be looked for in this direction, as in any case the creation and retention of conditions suitable to the life of the microorganisms, that is to say, the proper working of the vat, must always remain a matter of practical experience.

Plant for the Fermentation Vat.

Plant for the Fermentation Vat.

The vats should be placed in such a manner that neither those portions of them, which project above ground, nor those below the floor level are subject to any cooling influences. The fermentation process is best conducted by avoiding fluctuations of temperature as much as possible, and both for this reason and as a matter of economy, it is advisable to provide for the prevention of loss of heat and of any abnormal cooling, such as might result from subterranean water or a neighbouring watercourse.

The vats may be constructed of wood, iron, copper, or of brickwork lined with cement. Sheet copper isolated by masonry is the best material. The capacity of the vats varies from 100 to 3000 or more gallons; the smaller vats, however, are only used for dyeing on a small scale or in oriental countries. For general dyehouse purposes vats of 1500 to 2500 gallons are best employed. Large vats are most easily managed, as they are least liable to be upset by errors in the addition of the usual ingredients.

The vats are generally cylindrical, but occasionally rectangular in shape, and are sunk into the ground; for ease of working about a yard projects above the floor level.

They are preferably heated by indirect steam, the closed coil being about half way up the vat. Direct steam disturbs the sediment too much, and may also contaminate the vat with oil. Heating by fire is antiquated, and is now employed for small vats only, which in this case are of iron or copper, and constructed in the form of a cylinder tapering towards the bottom. They are encased in brickwork, space being left between the vats and the casing for flues leading into the chimney.

---

* German patent No. 30449.

The vats are usually stirred by hand by means of long rakes, but in large works mechanical stirrers are also employed. These consist of a stirring arrangement with horizontal wooden arms, which pass close to the bottom of the vessel and raise any sediment. The stirrer, which remains in the vat, is driven by means of a removable axle and cog-wheels fixed above the vat.

Suitable Indigo Brands for the Fermentation Vat.

Indigo Brands for the Fermentation Vat.

Before passing on to the details of working fermentation vats, we will first of all discuss the special brands of indigo put on the market for this purpose by the *Badische Anilin- & Soda-Fabrik.*

In those cases where duty or freight impose no restrictions, the paste brand

Indigo pure B. A. S. F. paste 20 % S

is recommended.

Of dry brands the following may be employed:

Indigo pure B. A. S. F. powder SL,
» » » powder S,
» » » lumps S,

in all of which the indigo is in that fine state of division necessary for the fermentation vat, and they consequently fulfil the prime condition necessary for an easy and ready solubility.

In addition we manufacture the following brands for special purposes:

Indigo solution B. A. S. F. 20 %,
Indigo vat » 60 %,
Indigo white » E extra,
Indigo pure » paste 40 % R,
» » » powder R,

the manner of application of which is explained in later chapters. The most convenient form is afforded by the paste brands, which, without any previous preparation, are added direct to the vat.

Indigo pure B. A. S. F. powder SL possesses the property of very easily forming with hot water a uniform paste, which does not settle even on standing for some length of time.

Mixing is best performed in a cask or similar vessel. Add the necessary quantity of boiling water, then strew in the indigo powder, and close with a well fitting lid, which, if necessary, can be packed with cloths.

The rising steam moistens the indigo and prevents its dust from flying about; a part sinks in the water, and, after 10—15 minutes, the remainder can be easily incorporated by stirring with a broom of twigs or wooden pole. The paste is stirred for a few minutes until quite uniform, and is then ready for use.

For a vessel the size of a petroleum cask 20 lbs. Indigo pure powder SL and 10 gallons hot water may be taken.

Indigo pure powder S and lumps S are less often employed. They are less bulky than the powder SL, but must be ground up in an indigo mill for some hours previous to use. To every pound of the above brands of indigo add 1 quart of water, in which is dissolved about $^1/_3$ oz. solid caustic soda. This latter facilitates the grinding.

Vat Recipes.

Vat Recipes.

We shall confine ourselves to giving only typical examples of recipes such as are used to-day on an industrial scale, and may be considered representative of the two chief forms of vat, the woad and the soda vat.

The kind of ferment and its quantity must in all cases be chosen to suit local conditions, but all the processes are the same in principle, so that our remarks are of general application.

a) Soda Vat.

Capacity 1300—1800 gallons.

Indigo pure paste 20 % S	24 lbs.
Syrup	16 »
Bran	40 »
Soda ash	28 »
Quicklime	6 »
Madder	12 »

Small vat, capacity about 50—60 gallons.

Indigo pure paste 20 % S	1	lb.
Bran	1 3/4	»
Syrup	3/4	»
Madder	6	oz.
Soda ash	11	»
Quicklime	1	»

The vat is worked with syrup, bran and lime, when required, and occasional additions of soda.

b) Woad or Bastard Vat.

Capacity 1300—1800 gallons.

Indigo pure paste 20 % S	24	lbs.
Woad	50	»
Bran	40	»
Soda ash	16	»
Quicklime	6	»
Madder	30	»

Or for a weaker vat of 1000 gallons capacity.

Indigo pure paste 20 % S	12	lbs.
Woad	50	»
Bran	20	»
Madder	20	»
Soda ash	8	»
Quicklime	2	»

A small vat, capacity 50—60 gallons.

Indigo pure paste 20 % S	1	lb.
Woad	2	lbs.
Bran	1	lb.
Madder	1	»
Soda ash	1/4	»
Quicklime	2	oz.

c) Old Woad Vat.

Still used in England.

Capacity 1800—2000 gallons. (For dark blue.)

Indigo pure paste 20% S	40	lbs.
Woad	100	»
Bran	20	»
Soda ash	10	»
Quicklime	6	»
Madder	20	»

Is worked with the addition of bran and lime and a little soda ash.

The stated quantities can be varied within wide limits, and equally good results are obtained by using less of one ferment and correspondingly more of another.

To set a fresh vat, well clean out the vessel, and fill with water, which may be hard or soft. Heat to 140° F., and add the ingredients in any convenient order. The woad should be previously broken up into small pieces and soaked for several hours in warm water (not above 160° F.). Carefully and thoroughly stir the vat, cover it with a well fitting lid, and spread over it cloth, sacks, etc., to prevent cooling and access of air. Then allow to stand.

Fermentation sets in, as a rule, within 12—16 hours, and it is important that, as soon as it starts, the vat should be sharpened with lime. It is, therefore, advisable to set the vat in the afternoon, so that sharpening is not necessary during the night. At the proper time the vat is uncovered, and, as soon as the originally bluish red liquor has become greenish, and the vat has developed a sweetish smell, freshly slaked and sieved lime is added in small portions, and the vat well stirred for 2—5 minutes according to its capacity. The stirring is repeated at intervals of two hours or so, and lime is added as required. The colour of the liquor slowly changes from green to yellow; when poured out of a ladle, a more or less dark coloured scum, the "flurry," appears on the surface, and the sweetish smell gives place to a sharper, more penetrating odour resembling herring roe.

The quantity of lime required for sharpening can only be determined by experience; on this point nothing definite can be said. The dyer recognises the state of the vat by its smell, and regulates the amount of lime accordingly.

Phenol-phthalein paper affords an excellent means of controlling the quantity of lime, for when dipped in the liquor it turns pale pink to red according to the amount present. Soda ash, however, also has the same effect, so that in a vat containing this salt the lime cannot be checked by such means. In doubtful cases, when an opinion as to the state of the vat cannot be formed from its smell, or when it has in some way got out of order, this paper is useful for ascertaining whether the vat is alkaline (either from lime or soda) or not.

A freshly set vat is usually ready for dyeing in two to three days. The surface of the liquor will have become covered with a dark blue flurry, which when removed exposes to view the yellow vat liquor, and this quickly becomes covered with a network of blue veins in a state of continual motion. Fermentation has become slow, and should only just be maintained. On a portion of the flurry being skimmed off, it should at once form, again, and when some of the liquor is poured out from a ladle, the flurry should stand up well, and the last drops poured out should slowly become green and then blue. The vat liquor ought to be clear and yellow, and the sediment of a similar colour and granular. The best test for determining whether the vat is ready for dyeing, is to dye a handful of wool, which should come out greenish yellow, and after being squeezed through rollers should slowly turn blue on exposure to air, and not lose greatly in depth on soaping.

For the first few days only one or two lots should be dyed daily. Before it can be regularly used, the vat must attain a proper concentration by being fed, and must have a certain mellowness, which will be the case in about one week after setting. The soda and woad vats demand slightly different treatment when being replenished. They are heated to 120—130° F., 16 lbs. of Indigo pure paste 20% S (or a corresponding amount of powder or lumps) added, and also to the soda vat about 6 lbs. of syrup, or to the woad vat 6 lbs. of syrup and 6 lbs. of bran. The well covered vat, after being carefully raked up, is allowed to stand for about 3 hours, again stirred, and the fermentation regulated for the night by the addition of lime as required. The following day the vat is sharpened with lime, and dyeing commences. If necessary, the vats are examined during the night, and stirred and sharpened with lime as required. If the vat is in good condition, the addition of indigo can be increased to 20 or 30 lbs. at a time, together with the necessary quantities of fermenting agents, the amount being naturally regulated by the work to be done.

No generally applicable rules can be given with regard to working the vat after the first addition of indigo, each vat must be individually treated. Variations determined by local conditions and the work done occur in the behaviour of the vat and in the course of the fermentation process, and the dyer must himself determine in each case the additions and quantities necessary. Any experienced man will obtain good results in dyeing with Indigo pure S if he chooses the proper amounts of ferments, and exercises care when making additions of alkali.

The vat should not be worked too mild, or the dyeings will lose too much in milling; on the other hand, it must not be too sharp, as this hinders the indigo from being taken up, and the shades obtained are dull.

Working the Vat.

Working the Vat.

The working of the vat is usually arranged as follows: At 6 a.m. the vat is stirred and sharpened; dyeing goes on from 8—11 a.m.; if necessary, it is again sharpened, and dyeing proceeded with from 1.30—4 p.m. Occasionally sufficient lime is added in the evening, so that dyeing can be commenced first thing in the morning, but this method of working demands great experience, because, on the one hand, the addition of lime must not be so great as to check fermentation, whilst, on the other hand, the vat must be sufficiently sharp next morning to prevent evolution of gas during dyeing.

In the afternoon, after dyeing, the vat is replenished with indigo and ferment and heated to 120—130° F. At night the fermentation is regulated by stirring up and springing. To sharpen before heating up is not permissible. Twice a week about 4 lbs. soda ash are added both to the woad and to the soda vat.

A dip lasts, as a rule, for 20—30 minutes, little additional dyestuff being taken up by prolonging the immersion. If, however, only a trace more dyestuff is needed to give the necessary depth of shade, and an extra dip would be too much, the duration of a dip may be extended at the outside to 45 minutes. Wool takes up indigo white from solution only until a certain equilibrium has been established. If deep shades are to be obtained, it is, therefore, necessary to convert the absorbed indigo white into indigo, and then by means of repeated dips to deposit further quantities of indigo in the fibre. It may be taken as a rule that a given shade produced by several dips in weak vats will be brighter and also faster than if obtained by rapid working in strong vats.

The woad or bastard vat produces on the first lots of wool a duller, greener shade of blue than the soda vat, owing to the colouring matters present in the woad and madder used for setting, but after a short time this difference disappears. For dyeing dark shades of blue the woad vat is preferable, but for light and bright shades the soda vat is more suitable.

When regularly worked, a vat can be run for about nine months; it should then be exhausted as far as possible, emptied, and set afresh. If the sediment in small vats accumulates to an inconvenient extent, it should be removed from time to time.

Reactions in the Fermentation Vat.

Reactions in the Fermentation Vat.

It will now be well to consider more closely the reactions, which take place in the fermentation vat, the working of which will be considerably facilitated, and disturbances more easily remedied, if the dyer has a clear idea of the mutual effect, which fermentation, sharpening, and dyeing exert on one another.

As has been previously mentioned, indigo is converted into indigo white by the hydrogen gas developed during fermentation. The indigo white is dissolved by the lime present or by the caustic soda formed by interaction of lime and soda ash, and from this solution it is taken up by the wool. The hydrogen entering into reaction cannot form gas bubbles, since it has gone to form indigo white, and the bubbles which are seen represent, therefore, so much in excess. Gaseous carbonic acid is also frequently formed, and it is, therefore, usual to differentiate between visible and invisible fermentation. To make sure that sufficient hydrogen is generated, the fermentation is so conducted that an excess of the gas is formed, which keeps the vat slightly active.

The caustic lime used for sharpening exerts a threefold action. In the first place, according to the quantity present, it checks the fermentation or even entirely suppresses it. It further neutralises the acids produced, and, as previously mentioned, reacts with soda ash to form caustic soda and carbonate of lime. Consequently, on the bottom and sides of old vats there is a copious deposit of calcium carbonate.

We see, therefore, that a very active vat necessitates more lime for its neutralisation than one in which the fermentation is less vigorous, and that large additions of indigo and ferment require correspondingly increased quantities of lime and soda.

Having regard to the action of the caustic lime, we can appreciate the effect on the condition of the vat, which too much or too little of this regulating agent will exercise. Too little lime permits fermentation to become violent, the acids generated are not neutralised, sour fermentation sets in, and the formation of hydrogen can become so energetic that the indigo white is partially or wholly destroyed. On the other hand, an excess of lime paralyses the activity of the bacteria, and interrupts fermentation, with the result that hydrogen is no longer generated, the indigo white is re-oxidised to indigo by the action of the air, and the liquor and sediment become green or even black.

From the above remarks it is clear that practical experience is absolutely necessary if a fermentation vat is to be rationally and economically worked, and its productive capacity utilised to the fullest extent. It is also now apparent, why it is impossible to describe all details or to make hard and fast rules appertaining to the working of a fermentation vat.

Various disturbing influences may make themselves felt in the working of the vat, and may cause great inconvenience and diminish the working capacity.

When a vat is freshly set or replenished, it may happen that the solution of the indigo is delayed through the addition of more dyestuff than the vat can deal with in the usual time. The quantities of fermenting agents given in the recipes are, therefore, intentionally liberal, because a large amount of sediment is a good breeding ground for the bacteria, which serve for keeping up the vat, and enables them during dyeing and stirring up to resist more easily the oxidising action of air. To assist the liquor in such cases, and to bring the dyestuff into solution, the vat is heated to 130 ° F., a few pounds of syrup and bran are added, the whole stirred, and then allowed to stand until gas is evolved, whereupon lime is cautiously added until the liquor and sediment show the normal yellow colour.

An indispensable condition for the successful progress of the fermentation is the maintenance of a proper temperature, which, even during dyeing, should not sink below 110° F., and care must, therefore, be taken that the vats do not cool down too much, *e. g.,* through water leaking through the foundations, or through insufficient isolation. Vats in cold rooms must be heated in the evening (but in no case over 140° F.), so that during the night and while being worked the temperature does not sink below 110° F.

If at the commencement of the day's work the liquor is green and not clear, sharpening must either be omitted altogether or but very little lime added, and dyeing must be stopped. Frequent stirring, maintenance of a proper temperature (130° F.), and waiting will best remedy matters in this case. Before sharpening gas must, of course, be freely issuing from the vat liquor.

The commonest source of trouble is over-sharpening of the vat, which may occur even with the most experienced indigo dyer. It is recognised by a penetrating smell, a weak flurry, and the dark brownish yellow colour of the vat, which on further sharpening turns green or blue. The results are dull shades, slow dyeing, and considerable washing off of the dyestuff. If the over-addition of lime has been small, and the vat is not yet green or blue, the excess can be removed by dyeing a few lots of wool, or by waiting for a day. If this does not improve matters, fermenting agents, such as bran or syrup, must be added. Should a still larger excess of lime be present, the effect of the fermenting agents can be strengthened by at first confining their action to a small area. This is done by putting bran in a sack, weighting it, and sinking it in the vat. The bran thus heaped at one spot soon sets up acid fermentation, and causes the excess of lime to be neutralised; gas is generated in the sack, which ultimately rises to the surface, a sign that the bran is used up. If necessary, the operation is repeated with a fresh bran sack. As previously mentioned, phenolphthalein paper is an excellent medium for ascertaining the decrease in the amount of caustic lime present, and whether a suitable degree of alkalinity has been reached.

In very unfavourable cases it may happen that the sharpening has been so excessive that fermentation cannot be started by the means described, or at any rate only after the lapse of some days. Artificial measures must then be resorted to, and the caustic lime neutralised by acetic or sulphuric acid, which must be very cautiously added, particular care being taken that the vat does not become acid. The acid must be added in a very dilute state and in small portions at a time stirring well, until phenol-phthalein paper is only coloured a faint pink by the liquor. Bran and syrup are then introduced, and, as a rule, fermentation sets in over-night. The vat must be carefully sharpened the following morning. It may be mentioned that to correct a moderately over-sharpened vat about a quart of sulphuric acid 168° Tw. per 1000 gallons liquor is required.

By working the vat with insufficient lime, or if the alkali has been neutralised by dyeing too many lots of white wool or of carbonised material still containing acid, it will become too mild. This is indicated by the sweetish smell, by the rapid oxidation of the dyed wool or of a drop of the liquor, and by the condition of the flurry, which breaks up und separates when vat liquor is poured from a ladle. The surface of a mild vat is characterised by showing broad instead of fine veins, and, when blown upon, the blue spot, which is typical of a vat in good working order, fails to appear. Provided soda ash has not been added a short time previously, phenol-phthalein paper will not be reddened by the liquor. Too mild vats do not dye well, and, after a few lots of wool have been passed through, turn green. Furthermore, there is the risk that fermentation may set in during dyeing, causing the wool to rise to the surface or to become stained by particles of the sediment. Shades obtained in mild vats are not of good fastness to milling. To remedy the defect the vats must be well sharpened, and in order that they shall not become too mild during working hours, thus causing stoppages, care must be taken that a thorough sharpening is given first thing in the morning. The vats should stand a shade on the sharp rather than on the mild side. The colour of a vat in proper condition is more of a brownish yellow, while a too mild vat is a pure bright yellow. Phenol-phthalein paper should be coloured pale pink by the vat.

The greatest danger to be feared when a vat becomes too mild is that fermentation will be so energetic that a partial or total decomposition of the indigo white may be brought about. This phase, which is known as a "runaway vat," occurs but seldom, and then as the result of insufficient attention. It tends to happen especially in the case of freshly set vats and vats which have been exhausted of dyestuff. A strong evolution of gas is not a necessary accompaniment, indeed it may happen—and these are by far the most dangerous cases—that the indigo is destroyed without any signs of gas being given off, and those vats are most liable to the fault which, through the addition of too little lime, are alkaline with soda ash only. A vat which is commencing to "run away," develops a sourish or foetid smell, the flurry becomes lighter and lighter and does not hold together, white flakes appear on stirring, and the sediment is slimy. As soon as these signs are noticed lime must be added in fairly large portions at intervals of from half to one hour, and the vat well stirred until the unpleasant smell has disappeared, or, if a strong evolution of gas takes place, until this has ceased. If the runaway vat does not contain soda nor react with phenol-phthalein paper, lime is simply added until the paper is slightly reddened.

If the working of a vat be stopped, it should be very well sharpened and allowed to cool, since a warm vat which is not worked is difficult to keep in order. On resuming work it is well stirred, heated to 140° F., syrup and bran added, and the vat left until fermentation sets in; should this not be the case after 12—24 hours, the excess of lime is carefully neutralised with acid, using phenol-phthalein paper as a means of control.

The Suint Vat.

Suint Vat.

In Hungary and the Balkans the suint vat, which in its working is somewhat similar to the fermentation vat, is used on a small scale and in the home industry. In this form of vat indigo is converted into indigo white by the action of the suint in weakly alkaline solution, the process being probably one of putrefaction combined with the formation of hydrogen. As raw, unscoured wool is generally employed, the washing and dyeing of the wool are effected in one operation.

The suint vat works very slowly, but, owing to the gradual manner in which the dyestuff is taken up by the fibre, even the darkest shades are very fast to rubbing and milling. There are two methods of operating. Either raw wool, direct from the sheep, is treated with unreduced indigo and alkali, or spun or woven wool is dyed in a vat set with the scouring liquor from raw wool. Fresh vats are not set, but old vat liquor is always used again. The alkali employed is wood ashes (potash) or a lye of wood ashes and lime; in certain exceptional cases, *e. g.*, in Greece, the vat is worked without any addition of alkali, the potash contained in the suint and the ammonia formed during putrefaction affording all that is required.

Indigo pure B. A. S. F. lumps 60% or 40% are the most suitable brands for the suint vat.

The following is a detailed working description for unscoured wool: A copper vessel of about 100 gallons capacity is filled three quarters full with liquor from an old suint vat, which is then heated to 120—140° F., and about 14 gallons wood ash lye 9° Tw. or a corresponding amount of potash are added. Phenol-phthalein paper should then be slightly reddened by the liquor. A sufficient quantity, say ½ to 1 lb. of Indigo pure B. A. S. F. 60% lumps is rubbed into a paste with old vat liquor and introduced into the vessel; 100 lbs. of raw wool are then entered, and a cover placed over the vat, which is allowed to stand for 48 hours. During this time the indigo is reduced, and the wool, which is being scoured at the same time, absorbs the indigo white produced. After wringing out and oxidising, the wool is, if necessary, again passed through the vat. Potash or lye is added as required, so as to keep the vat faintly alkaline. A large excess of alkali is strictly to be avoided.

Indigo Solution B. A. S. F., Indigo Vat B. A. S. F. 60%, and Indigo White B. A. S. F. *E* extra for the Fermentation Vat.

The two first mentioned preparations contain indigo already reduced in the form of the soluble sodium salt of indigo white, the latter is free indigo white. They offer the great advantage of considerably increasing the output of the fermentation vat. The loss of time due to the necessity of bringing the indigo into solution by the gradual action of the fermentation process is avoided by their use. Again a vat can be kept up to one

Indigo solution B. A. S. F., Indigo vat B. A. S. F. 60%, and Indigo White B. A. S. F. E extra for the Fermentation Vat.

uniform strength without any stoppages worth mentioning, and thus the daily production may be increased, and pressing orders more easily executed.

The vat is best worked by feeding up as usual at night with ordinary indigo, which will be in solution in the morning. After sharpening the vat and using it for four or five dips, Indigo solution, Indigo vat 60%, or Indigo White E extra is added, and thoroughly and uniformly mixed with the vat liquor without disturbing the sediment more than cannot be avoided. As soon as the liquor is clear further dips may be given.

Indigo White E extra is previously dissolved in a little vat liquor and lime. Both Indigo solution and Indigo vat 60% are added directly to the vat, and when using the latter care must be taken before starting to ensure that no undissolved portions are swimming about on the surface. Since both brands contain the necessary alkali for keeping the indigo white in solution, less lime is to be taken for sharpening, and if the indigo is used exclusively in this form, smaller quantities of fermenting agents than usual are required for working the vat.

Indigo pure and Natural Indigo in the Fermentation Vat.

Indigo pure and Natural Indigo in the Fermentation Vat.

We have seen in the above description of the working of the vat that this is entirely dependent on practical experience. A process based on definite figures and recipes is impossible in the case of the fermentation vat. It is, therefore, obvious that a dyer can work more accurately with an indigo brand of uniform quality than with a dyestuff which, both as regards its composition and its physical condition, is liable to vary. Hence Indigo pure owing to its regular strength and its definite qualities offers great advantages over natural indigo, the quality of which varies with every crop. The brands most commonly used, Indigo pure B.A.S.F. paste S and Indigo pure B.A.S.F. powder SL, are ready for use and do not require the tiresome and costly grinding of vegetable indigo.

The purity of synthetic indigo facilitates the conduct of the vat, permits of uniform working, and relieves the dyer of the irregularities and inconveniences caused by the varying qualities of the natural product. The whole of the work is rendered more accurate, and calculations become more reliable.

Indigo pure and natural indigo behave in much the same manner in the fermentation vat, so that every experienced dyer can use the synthetic product without difficulty. A small but unimportant difference is that in the case of natural indigo fermentation sometimes proceeds more energetically than with Indigo pure, and, consequently, the vat has to be more strongly sharpened. Specially is this noticeable with inferior kinds, such as Kurpah, Madras, and Guatemala, but it is less so with Bengal, and not at all with the best Java varieties. It is due to the fact that the natural product contains vat bacteria due to the process of manufacture. The solution of natural indigo is not thereby made quicker or easier, for Indigo pure, whether used for setting afresh or feeding up a vat, goes into solution in the normal time as easily as natural indigo. The fact has to be borne in mind, however, that vegetable requires more lime than synthetic indigo, and in comparative trials care must be taken that the vats are in an equally alkaline condition, *i. e.,* that they are of the same degree of sharpness.

To obtain a proper and reliable idea of the economic and other advantages of Indigo pure over the natural product, it is best to make comparative dyeings on the large scale of both products on a price basis, working under exactly similar conditions. Estimation of the indigotine in one or several lumps, and also analysis, give results which are only to a certain extent correct, since in the same chest the indigotine in different lumps may differ even by 10%.

For comparative trials freshly set vats should not be taken, as they are subject to disturbances, and the results may not be altogether reliable. It is best to employ two vats as near to one another as possible and similarly situated, which have been brought into normal working order. These vats should be worked for a few days until they are equally strong, and then fed with equal values of the indigo brands to be compared. The vats are kept regularly at work for one to two weeks, and the woollen material to be dyed always divided into two equal parts, so that similar quantities of the same shade are compared. The relative value of the dyestuffs is determined by comparing the quantities of wool dyed in the two vats.

3. The Hydrosulphite Vats.

General Remarks.

Development of the Hydrosulphite Vat.

The hydrosulphite vat was first recommended by *Schützenberger*[*] and *Lalande,* who in 1871 patented in England a process for printing and dyeing with indigo and hydrosulphite. The hydrosulphite vat was first employed for wool dyeing in England, where it is still largely used in its original form, in which a mixture of zinc dust and bisulphite acts as the reducing agent, and lime as the solvent for the indigo white. On the Continent, however, the hydrosulphite vat, whether as zinc-bisulphite vat or hydrosulphite-soda vat free from sediment, has never established a firm position, and the fermentation vat still holds the field.

Various causes tended at one time to bring the hydrosulphite vat into discredit with wool dyers. The preparation of the vat from the materials then available was difficult, as small variations in its composition may lead to bad results. The dyer was not only obliged to reduce the indigo himself, but he was confined to the use of assistants, which could not be depended upon for uniform quality and under certain circumstances injuriously affected the wool. Hydrosulphite, whether prepared on the spot or bought in the ready-made liquid form, was unreliable, owing to its rapid deterioration and the consequent impossibility, or at any rate difficulty, of determining the quantity required. To dissolve the reduced indigo, it was necessary to use either caustic soda or lime, and in the latter case a clear vat free from sediment was not obtained. Since a slight excess of these alkalies may injure the fibre and affect the shade obtained, and since in the case of the hydrosulphite vat such excesses cannot be readily detected, as they can in the fermentation vat, it is obvious that a great deal of damage must have been done. On account of the retarding or even stripping influence which too much alkali in the hydrosulphite vat exercises, the opinion became wide spread that this vat was not suitable for dark shades.

In addition to the causes of a chemical nature mentioned above, the adoption of the hydrosulphite vat was retarded by the lack of attention given to the mechanical side of the subject.

---

[*] See page 124.

The importance of removing the excess of dye liquor from the fibre immediately after dyeing was not realised, and consequently squeezing rollers were, as a rule, considered unnecessary. The hydrosulphite vat was worked in a manner similar to that employed for the fermentation vat, the fundamental difference between the two not being taken into account. The fermentation vat is, as a matter of fact, merely a solution of indigo white, and the reduction is mainly effected in the sediment; the hydrosulphite vat, on the other hand, contains in solution, besides indigo white, an extremely energetic reducing agent. On being removed from the vat, the fibre contains both indigo white and hydrosulphite; the latter, if present in excess, prevents either partially or wholly the oxidation of the wool by the air or even strips colouring matter from the fibre. The result of this is unlevel dyeing, and in the case of loose wool the so-called "white tips," and the stronger the vat the more noticeable are these defects. When light shades are dyed in weak vats, this fault is less apparent, and, for this reason, the employment of the hydrosulphite vat was confined to the production of light shades.

The hydrosulphite vat could only receive the recognition it deserved when reliable and non-injurious materials for its preparation were put at the dyer's disposal. This was brought about when the *Badische Anilin- & Soda-Fabrik* introduced its Hydrosulphite powder conc., a reducing agent, which permits of accurate working of the vat, and when the use of injurious solvents was abandoned.

To facilitate this latter object, the *Badische Anilin- & Soda-Fabrik* has put on the market a product containing indigo in the form of ready reduced indigo white entirely free from caustic alkali, the only free alkali being ammonia, which has no injurious effect on wool. This is

Indigo solution B. A. S. F. 20 %,

a product, which has met with great success in the wool dyeing industry, and in conjunction with

Hydrosulphite conc. B. A. S. F. powder (pat.)

is employed in the preparation of the

Hydrosulphite-ammonia Vat.

Hydrosulphite-ammonia Vat.

In simplicity and accuracy of working, productivity and quality of results, this form of vat surpasses all others. Indigo solution B. A. S. F. may be looked upon as a ready-made, stable stock vat, which, unlike stock vats prepared in the dyehouse, is free from all injurious alkali, such as caustic soda or lime. The same product is also supplied by us in solid concentrated form as

Indigo vat B. A. S. F. 60 %,

Indigo vat B. A. S. F. 60 %.

which, however, we recommend only in those cases, where dyeing is confined to occasional small lots, or where duty and freight charges tell against the employment of Indigo solution 20 %.

In Indigo solution B. A. S. F. 20 % and Hydrosulphite conc. B. A. S. F. powder the dyer has two products ready for immediate use, the composition of which remains constant, thus permitting of working almost exactly according to a definite recipe.

Two factors play an important part in working the hydrosulphite-ammonia vat, namely, the addition of glue and the use of squeezing rollers for freeing the dyed goods from excess of liquor. We have already indicated the importance of this last point, and will now explain the function of the glue.

As stated, ammonia is the only alkali necessary for working a vat set with Indigo solution B. A. S. F. and Hydrosulphite conc. powder, but this is so mild an alkali that, of itself, it is incapable of keeping in solution the indigo white contained in the vat. It is, however, absolutely necessary, if fast and satisfactory dyeings are to be obtained, that no undissolved indigo white should be contained in the vat, and means must, therefore, be devised for keeping indigo white in solution without the aid of caustic alkali. We have discovered in the course of our investigations* that glue and similar substances possess the remarkable property of keeping indigo white in exceedingly fine colloidal suspension practically equivalent to solution in a hydrosulphite vat containing free ammonia and no stronger alkali. In this condition indigo white dyes exceedingly well, and when afterwards oxidised leaves the dyestuff well fixed. The glue, of which only small quantities need be taken, has no injurious effect, nor is its use attended with any inconvenience.

Contrary to the bisulphite-zinc-lime vat, the hydrosulphite-ammonia vat, prepared with Indigo solution B. A. S. F. 20 % and Hydrosulphite conc. powder B. A. S. F., contains no sediment, and thus permits of the employment of smaller vessels or the full utilisation of larger vessels. Loss of dyestuff, due to indigo white remaining in the sediment, is avoided, and the complete absence of sediment permits of greater production, since after replenishing or springing the vat it is not necessary to wait for sediment to settle.

---

* English patent specification No. 8510 (1902) and German patent No. 152907.

Our hydrosulphite-ammonia vat is also very economical to work, since practically no loss of indigo takes place during reduction, whereas in the case of the zinc-bisulphite vat the destruction of a certain amount of dyestuff cannot be avoided, and under some circumstances, *e. g.,* if the stock vat stands too long or with careless working, this loss may be even 20% or more.

Hydrosulphite Vat and Fermentation Vat.

Before describing in detail the working of the hydrosulphite-ammonia vat we may compare it briefly with the fermentation vat, since it is important to many consumers to know which of these two vats is to be preferred in a given case and most fully satisfies their particular requirements.

Considering first the influence of the vat on the quality of the woollen material dyed, we have already seen that our hydrosulphite-ammonia vat contains as alkali only the absolutely harmless ammonia, whilst in the fermentation vat quicklime is employed. Even though a certain excess of the latter can be immediately recognised by the dyer, cases frequently occur, in which the vat becomes sharper than was intended, and contains more alkali than is good for the wool. As a consequence of this, wool dyed in the fermentation vat is, as a rule, harsher and less "lofty" than wool dyed in the hydrosulphite-ammonia vat.

A further factor tending to influence the quality of the wool is the employment of squeezing rollers, which is only practicable in the case of the hydrosulphite vat for the following reason: The greater part of the liquor running from the squeezing rollers back into the vat is oxidised, that is to say, it contains a considerable amount of precipitated indigo. This is immediately re-reduced to indigo white by the hydrosulphite present in the vat, and the latter, therefore, remains in good working condition. It is otherwise with the fermentation vat, which cannot in a brief space of time reduce the precipitated indigo, since it does not contain a strong reducing agent like hydrosulphite, but is dependent on the slow process of fermentation. The employment of squeezers would, therefore, soon make the fermentation vat unworkable through the accumulation of undissolved indigo, and would also diminish its productivity, which is in no case great. For this reason it is almost everywhere usual to work the fermentation vat without squeezing rollers, but since it is unavoidable that the dyed wool should take out of the vat a quantity of liquor, and consequently of unfixed dyestuff, the wool is not so clean and less easily spun than such as has been dyed in a hydrosulphite-ammonia vat provided with squeezing rollers.

In the hydrosulphite vat a much larger amount of work can be turned out, and this brings us to a consideration of the economical side of the question. We have seen that in the fermentation vat the solution of indigo is slow and is liable to various unforeseen disturbances and interruptions, whilst the hydrosulphite vat is dependent on a rapid and purely chemical process. A hydrosulphite-ammonia vat prepared with the aforementioned products of the *Badische Anilin- & Soda-Fabrik* is ready for use in half an hour, and can at once be worked to the fullest extent. By replenishing with indigo solution and hydrosulphite it can be kept in good working condition and used continuously for dyeing from early morning until late at night. The case is different with the fermentation vat, which after setting requires two full days before it can be worked at all, and several days before it can be worked regularly. Under favourable circumstances, when the vat is in a healthy condition, only a limited number of successive dips can be given, and the vat must be then left for several hours to rest and settle. For this reason the production from a hydrosulphite vat is far greater than from a fermentation vat of the same size. It can be taken that from a hydrosulphite vat containing 500 — 660 gallons, in which 50 lbs. of wool are dyed at a time, 250 lbs. of dark blue, dyed in three dips, will be obtained in a day of ten hours, whilst a fermentation vat of 1800 gallons, also dyeing 50 lbs. of wool, will only turn out, in the same time, about 70 lbs. of an equally dark shade.

The plant for a hydrosulphite-ammonia vat is much simpler than for a fermentation vat, because of the amount of sediment contained in the latter, and the large volume of liquor necessary for working, which also requires more steam to heat it.

In cases, where it is above all necessary to economise in time, space, and labour, the hydrosulphite vat is thus unhesitatingly to be preferred.

With regard to cost for materials the advantage is on the side of the fermentation vat, as hydrosulphite and ammonia are more expensive than ferments. The extra cost of material is, however, in part counterbalanced by the fact that in the fermentation vat there is a considerable loss of indigo. The fermentation process may destroy a greater or less proportion of the indigo, but hydrosulphite, even when present in excess, is perfectly harmless in this respect. Further, the removal from the wool of superfluous liquor by squeezing effects an economy, since less dyestuff is lost during washing and milling.

The hydrosulphite vat is simpler in its application, and is easily adapted to varying demands as regards shade, since without loss of time it can be strengthened by feeding with indigo or exhausted by dyeing. The fermentation vat is, by comparison, unwieldy, the indigo added is but slowly dissolved, only a limited number of dips can be given in succession, and, after being stirred, time must be allowed for the sediment to settle. The fermentation vat is consequently better adapted for those dyehouses, where, both as regards shade and quantity of work, conditions are uniform, and forced production is not demanded.

The fermentation vat cannot be used for machine dyeing on account of its sediment and its sensitiveness to air. For this purpose the hydrosulphite-ammonia vat, which is perfectly clear, is best employed. For piece dyeing the fermentation vat is so far preferable in that it better penetrates thick or heavily milled goods, but the penetrative powers of a hydrosulphite vat can be increased by frequently passing the goods under the liquor through squeezing rollers.

As regards the shades produced by the two vats, pale and medium shades are much the same in whichever vat they are dyed, except that the hydrosulphite-ammonia vat produces somewhat brighter results. But deep shades dyed in the hydrosulphite vat have more body and are blacker when looked at "down," whilst those dyed in the fermentation vat possess a coppery hue. During carbonisation and decatising these differences tend to disappear, they can, however, still be recognised in the finished goods, and are the more noticeable the greater the difference in the number of dips given to obtain a similar depth of shade. They are presumably due to the indigo of the hydrosulphite vat being deposited in the fibre in a finer state of division than is the case when the fermentation vat is employed.

We will now describe in detail the various forms of hydrosulphite vat.

The Hydrosulphite-ammonia Vat.

The brands of indigo suitable for this kind of vat are

Indigo solution B. A. S. F. 20%,
Indigo vat B. A. S. F. 60%.

Hydrosulphite-ammonia Vat.

Fig. 11 shows a sketch of a machine* used for dyeing loose wool in the hydrosulphite-ammonia vat. The dye vat is constructed of tin plate, sheet copper, or stout wooden staves 1—2 inches in thickness. Ordinary sheet iron can be used, but is very liable to rust, which, besides leading to the rapid deterioration of the vessel, also affects the vat liquor. Wood, although less durable than metal, protects the liquor better from loss of heat.

The necessary capacity can be determined on the basis of 10 gallons of liquor for every 1 lb. of wool dyed, and as it is not advisable to work the wool in lots of more than 60 lbs., the maximum capacity will be about 600 gallons. For lots of about 40 lbs., the vessel, which should hold a little over 400 gallons, should have the following dimensions: 6 ft. 6 in. long, 3 ft. 6 in. deep, 3 ft. wide. The wool to be dyed is contained in a perforated basket, made of tin plate or sheet copper, or of tinned iron or tinned copper wire; this basket revolves about an axle and can be raised out of the vat by means of a wire rope and winch. For squeezing the wool after dyeing a pair of ordinary iron rollers fitted with regulating springs, such as are used on wool washing machines, is employed. The rollers have a diameter of 8 — 12 inches; the upper one is evenly covered with a layer of strong cord, over which is wrapped slubbing or strips of cloth. An endless apron on either side of the rollers serves for the conveyance of the wool to and from the machine. A slanting tin gutter conveys the liquor back to the vat. The wringing

---

* Dyeing machines are supplied by *H. Krantz,* Aix-la-Chapelle; *Eduard Esser & Co. G. m. b. H.,* Görlitz; *Wagner & Hamburger,* Görlitz.

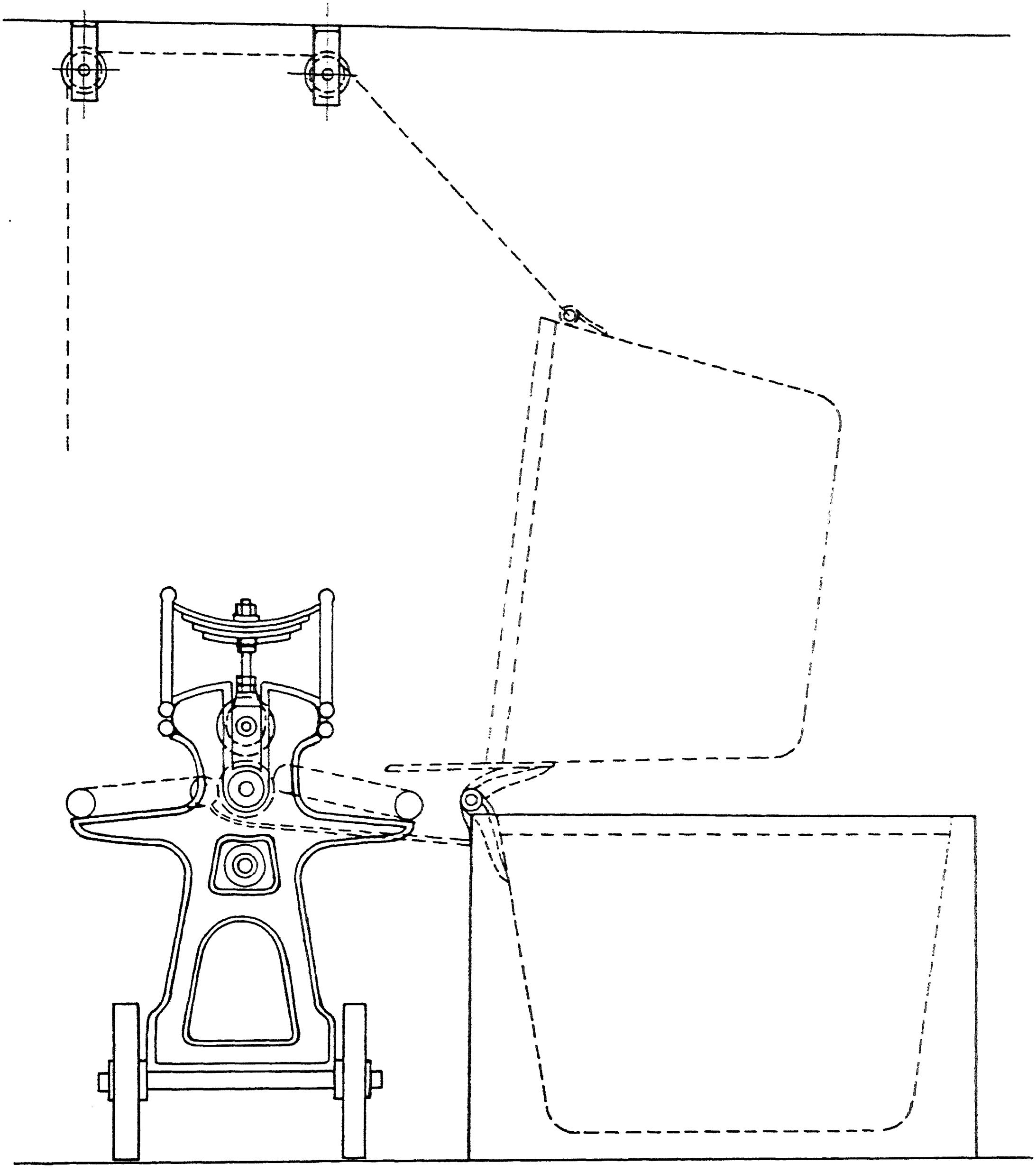


Fig. 11. Apparatus for the Hydrosulphite Vat.

machine may be fixed to the vat, but it is preferable to have it separate and running on wheels, so that it can be used wherever desired. It is driven mechanically.

It is well to fit up the vats in a building where they are protected from extreme cold.

Working the Vat.

Working the Hydrosulphite-ammonia Vat.

The concentration of the vat depends on the depth of shade required and the number of dips in which it is to be obtained. To obtain well penetrated dyeings, as fast as possible to rubbing and milling, it is not advisable to dye too quickly, that is to say, to employ too strong vats, nor to complete the dyeing in too few or with too short dips. For pale shades the vat is set with ½—1 gallon Indigo solution B.A.S.F. 20% per 1000 gallons liquor; for medium blue in 2 dips and dark blue in 3—4 dips about 2½ gallons are taken. 5 gallons Indigo solution B.A.S.F. 20% per 1000 gallons liquor is to be considered the maximum, and with such a vat a dark blue can be dyed in 2 dips.

Indigo solution B.A.S.F. 20% and Hydrosulphite conc. powder are extremely convenient in their application. The former can be taken from the cask by means of a tap, and thus unnecessary contact with the air avoided, and our hydrosulphite greatly simplifies working in that it can be added directly to the vat. To prevent deterioration, it must be kept in dry, closed vessels protected from heat and damp, and for taking it out only dry scoops, etc., must be used. It is advisable to have measures of known capacity both for the indigo solution and for the hydrosulphite, so that it is unnecessary to weigh them out each time.

The glue solution is made by dissolving 1 lb. of ordinary glue in 1 gallon of water. The solution must not stand too long, or it will turn sour and decompose.

The following example will show how to set a vat of about 600 gallons.

Heat the water to 120° F., and add

2½ pints ammonia (17% NH_3) and
1½ lbs. Hydrosulphite conc. B.A.S.F. powder,

and after well stirring add

14½ pints glue solution (10%), and then
11 » (15½ lbs.) Indigo solution B.A.S.F. 20%.

After well stirring, the vat must be clear and of a greenish yellow colour. Enter the wool (about 50 lbs.) and work for 20—30 minutes with poles, taking care to keep the wool from contact with the air. The squeezing is performed by laying small lots of wool on the endless apron by means of wooden forks. In doing this the perforated basket must not be wound high enough to bring the wool saturated with vat liquor into contact with the air, but only so far as is necessary to conveniently and gradually remove it. Only when it has been completely emptied, should the basket be removed entirely from the liquor. The squeezing must be done quickly, and too large lots must not be put through the rollers at once, or incomplete and uneven removal of the liquor will be the result. When the vat is in the proper condition, white wool should be pale green when it comes from the vat, and gradually turn blue. From the squeezers the wool falls into baskets, where it remains until completely oxidised, which will be the case in 5—10 minutes. Meanwhile a second lot is entered into the vat, and the two lots are dyed alternately. The finished wool is merely rinsed with cold water.

The vat must remain clear and retain its greenish yellow or pale green colour while it is being worked. If it becomes dark green or bluish green, it must be sprung with hydrosulphite; usually about $^1/_2$ lb. suffices to bring the vat into the proper condition. This is strewn into the vat, and if after 15—20 minutes the right colour has not returned, a second portion is added. The quantity of hydrosulphite necessary for working the vat depends on the shade required. Pale shades necessitate the use of more hydrosulphite than dark shades, because fresh lots of wool are more frequently entered, and more air is consequently brought into the vat.

An extra addition of hydrosulphite is also necessary when dyeing dry wool, because this contains considerably more air than wool which has been wetted out. The more irregular the working of the vat, the more hydrosulphite will be needed in proportion to the work turned out, because during stoppages the hydrosulphite in the vat is being oxidised by the air. It can be reckoned on an average that, when working regularly, the amount of hydrosulphite necessary is one-tenth the quantity of indigo solution used.

The quantity of ammonia added must be just sufficient for the vat liquor to smell faintly of it and to slightly redden a strip of phenol-phthalein paper. In no case must the vat be allowed to become acid, as the hydrosulphite would then be rapidly decomposed. Ammonia is necessary for the production of fine, bright shades and increases the reddish cast of the dyeings, but it must not be added in excess, or the absorption of indigo white by the wool will be retarded. Hydrosulphite, when it exercises its reducing action, fixes a certain quantity of ammonia, and for this reason, when a larger addition of hydrosulphite is made, a corresponding addition of ammonia is called for. On this account, and also because wool withdraws ammonia from vat, it is clear that pale shades require more ammonia than dark and medium shades. The regular production of dark shades necessitates on an average a daily addition of from 1—2 quarts of ammonia, whilst for medium or sky shades about double these quantities will be required. When work is stopped, *e. g.,* when the vat is to stand over-night, it is advisable to add about 1 lb. hydrosulphite and sufficient ammonia (about 1 quart per 600 gallons liquor) to render the vat distinctly alkaline, so that it will redden phenol-phthalein paper. The ammonia increases the stability of the hydrosulphite, and the vat remains in good condition for several hours, or at any rate is more easily brought again into working order.

Glue solution need not be regularly added, and that used for setting the vat will suffice for several days. If the vat is kept in work for some time, 2 quarts of glue solution should be added twice a week.

The quantity of Indigo solution 20 % to be taken depends on the shade and the production. The vat should be replenished in such a way that it remains approximately of constant strength, and that a given shade is always obtained with the same number of dips of equal duration. A dyer will soon learn the quantity required.

The length of time a vat can be worked is determined by the extent to which it is worked, and the purity of the woollen material dyed.

When working at full capacity, it is advisable to renew the vat once a week, since the accumulation of salts and impurities from the wool affects the brightness of the shades obtained.

To exhaust a vat, omit the addition of ammonia, and enter, if possible, only fresh wool. The process can be accelerated by the addition of ammonium chloride (sal ammoniac), which has the power of throwing the indigo white out of its alkaline solution and on to the fibre. To a moderately strong vat add 1 lb., to a weak vat about $^1/_2$ lb. sal ammoniac previously dissolved in water.

The Hydrosulphite-soda Vat.

Hydrosulphite-soda Vat.

The hydrosulphite-soda vat differs from the hydrosulphite-ammonia vat in that indigo in paste or powder form is employed in place of Indigo solution 20 % or Indigo vat 60 %, and solution is effected by means of hydrosulphite and caustic soda. The solution thus prepared is called the "stock vat." We recommend this form of vat only in cases where the employment of the hydrosulphite-ammonia vat is for some reason precluded. It will yield good results when carefully and properly worked, and possesses in the entire absence of sediment and thorough utilisation of the colouring matter the same advantages as the hydrosulphite-ammonia vat over the zinc-bisulphite-lime vat to be described later. Since, however, the reduction of the indigo has to be performed by the dyer himself, the hydrosulphite-soda vat is more troublesome to work than the hydrosulphite-ammonia vat, and the employment of strong caustic alkali introduces the risk of damage to the wool fibre.

The most important rules to be observed in working the hydrosulphite-soda vat are

1. No more caustic soda is to be employed than is necessary to bring the indigo into solution.
2. It must be remembered that an excess of hydrosulphite in conjunction with caustic soda prevents dyeing, or even strips indigo from the fibre.

Good results depend on the vat containing a definite proportion of caustic soda, and the stated quantities of this alkali, the strength of which should be accurately known, must be adhered to. Since commercial liquid caustic soda is frequently impure, the actual amount of caustic alkali is not always accurately indicated by a hydrometer, and only such caustic should be employed as is of guaranteed strength. To maintain this strength, the caustic soda must be kept in a well closed vessel.

In preparing this vat only the minimum quantity of caustic soda necessary is employed, so that its action on the wool may be reduced to the lowest possible limit. Glue solution is added in this case as in the hydrosulphite-ammonia vat. Its function is to prevent the precipitation in the vat of indigo white in a difficultly soluble form, which might under certain circumstances occur, owing to the removal of the alkali necessary for solution from the vat both by the hydrosulphite and by the wool. As the glue solution becomes sour on standing, large quantities should not be made up at one time.

The following brands are suitable for this form of vat:

Indigo pure B. A. S. F. paste 20 % and 30 %,
» » » powder and powder L,
» » » pieces,

or, where preferred, the *S* brands may be employed.

The pastes can be added direct in making up the stock vat, the powder must be previously stirred into a paste, and the pieces must be wet ground.

Working of the Vat.

Working of the Hydrosulphite-soda Vat.

The remarks made when describing the hydrosulphite-ammonia vat as regards concentration are equally applicable in the present case.

To set the Stock Vat.

In a wooden vessel stir

15 lbs.	Indigo pure B. A. S. F. paste 20 % (or the corresponding quantities of other brands) with
3 gall.	hot water, and add
3 pints	caustic soda 77° Tw. (or 6 pints caustic soda 42° Tw.), and stirring well add in small portions at a time
3 lbs.	Hydrosulphite conc. B. A. S. F. powder,

and heat the mixture for ½ hour at 140—150° F. It should then appear yellow, should run off clear and yellow from a strip of glass, and ought not to show any dark spots. Should the latter appear, they indicate undissolved indigo, and hydrosulphite must be added in small portions until complete solution is effected.

If the stock vat is greenish white and turbid, undissolved indigo white is present owing to the use of insufficient caustic soda. In this case small quantities (about $^1/_2$ gallon) of caustic soda must be carefully added until the vat is quite clear. It is tested if properly alkaline with a strip of phenol-phthalein paper, which should just turn momentarily a pale pink.

To set the Dye-vat.

Heat the water to 140° F., add 1 quart ammonia (Sp. gr. 0·936 $= 17\,^0/_0\ NH_3$), and then about 5 oz. hydrosulphite to render harmless any dissolved oxygen. Now add 10 quarts glue solution ($10\,^0/_0$), and lastly the stock vat. The vat should now be greenish yellow and should not feel slimy, or it contains too much caustic. Phenol-phthalein paper should only turn a pale pink. Dyeing is carried out and the vat worked as described for the hydrosulphite-ammonia vat, but instead of indigo solution the stock vat as above prepared is employed.

When working regularly add $^1/_2$—1 quart ammonia daily, so that the liquor smells faintly of it.

The Hydrosulphite-lime Vat.

Hydrosulphite-lime Vat.

This vat differs from the previously described hydrosulphite-soda vat in that quicklime is employed in place of caustic soda. Lime being a weaker alkali than soda, there is less danger to the shade and to the wool fibre in its use, and the dyeings produced in the hydrosulphite-lime vat are finer and brighter. Nevertheless, the lime must be accurately weighed and no more employed than is necessary to dissolve the indigo white. Even a slight excess of lime retards the absorption of indigo white by the fibre and renders it less fit for spinning, making it hard and brittle. On the other hand, if insufficient lime is present indigo white will remain undissolved, and the fastness and evenness of the dyeings will suffer. The correct degree of alkalinity is ascertained by phenol-phthalein paper as described in the foregoing section.

Unlike the hydrosulphite-ammonia or hydrosulphite-soda vat, the hydrosulphite-lime vat contains sediment, which brings with it various disadvantages. It prevents the utilisation of the whole of the vat liquor, and takes up a certain amount of dead space; also losses are caused by indigo white being retained by the sediment, and the complete exhaustion of the vat is thus prevented. After replenishing with stock vat or hydrosulphite, the sediment has to be allowed to settle, which diminishes production, and finally, owing to the use of lime, wool dyed in this vat has to be soured.

The dyeing plant is the same as for the hydrosulphite-ammonia vat, except that, to provide for the sediment, the vessels must be deeper. The same indigo brands are employed as for the hydrosulphite-soda vat, and the vat is set in the same manner and with the same quantities of materials, but substituting $1^1/_2$ lbs. of quicklime for the 3 pints of caustic soda. Before adding the lime to the vat, it should be slaked and made into a smooth paste with water. Fresh quicklime, as pure as possible, should be taken.

The method of working the vat is the same as for the hydrosulphite-soda vat.

The Bisulphite-zinc-lime Vat.

Bisulphite-zinc-lime Vat.

In this form of vat the dyer himself prepares the hydrosulphite as required by mixing sodium bisulphite and zinc dust. The alkali employed for dissolving the indigo white is lime. The disadvantages of this form of vat compared with vats worked with our Indigo solution and Hydrosulphite powder have already been pointed out. Owing to the presence of lime, the shade and the fibre are exposed to the same risks as in the hydrosulphite-lime vat described in the preceding section. The mixture of bisulphite and zinc gives rise to an even larger amount of sediment with its attendant disadvantages. A further disadvantage inherent in the use of a mixture of bisulphite and zinc dust is that, during reduction or after, a certain amount (5 — 20 % or even more) of indigo is destroyed, which is not the case when ready prepared hydrosulphite is employed.

This loss is due to the almost unavoidable presence of zinc in the vat, and is increased by long standing of the stock vat or of a dye-vat into which particles of unchanged zinc dust have been introduced from the stock vat. The working of the vat as compared with the hydrosulphite-ammonia or hydrosulphite-soda vat is rendered more difficult by the acid nature of the zinc dust and bisulphite mixture, which neutralises a portion of the lime in the vat, and may thus bring about a precipitation of indigo white. Since, on the other hand, an excess of lime must be carefully avoided, it is not easy for the dyer to keep to the proper degree of alkalinity.

However, in spite of all defects the "bisulphite" vat is sometimes used, and we accordingly give a detailed working description.

The plant is the same as described for the hydrosulphite-ammonia vat, except that the vat must be about twice as deep on account of the sediment formed.

The same brands of Indigo pure B.A.S.F. may be used for preparing the vat as are suitable for the hydrosulphite-soda vat (page 255), and the following ingredients are also necessary:

1. Bisulphite 57° Tw. prepared by diluting commercial bisulphite liquor, *e.g.*, 3 gallons bisulphite 71—76° Tw. and 1 gallon of water.
2. Zinc dust.
3. Milk of lime 20%. 20 lbs. of good quicklime are slaked, made into a thin paste, and diluted to 10 gallons with water. It must be well stirred before use.

Stock Vat.

In a wooden cask provided with a lid mix together

20 lbs. Indigo pure B.A.S.F. 20%,
1 gall. hot water,
2 » milk of lime 20%,

and add a mixture of

2 1/2 gall. bisulphite 57° Tw.,
2 1/2 lbs. zinc dust.

The mixture is prepared by gradually adding the zinc dust to the bisulphite with gentle stirring, and allowing to stand until the colour is pale grey and the smell of sulphurous acid has disappeared.

When the whole has been well mixed, dilute to 12 1/2 gallons by the addition of hot water (140—150° F.) and allow to stand, stirring occasionally, until it has turned yellow with a coppery appearance on the surface.

Setting and Working the Dye-vat.

Heat the water to 120—130° F. and add a mixture of

2 quarts bisulphite 57° Tw.,
1/2 lb. zinc dust,

and after half an hour add the necessary quantity of the stock vat.

To every 200 gallons of vat liquor add one-eighth to one-half of the stock vat according to the shade required. Stir up, allow to stand one hour, and then commence to dye. The temperature should be 120—130° F., and the duration of the dips as previously mentioned.

When in proper condition the vat is greenish yellow; a bright yellow colour shows that it is too sharp, a turbid, green or blue-green appearance that insufficient reducing agent is present. In the latter case dull and poor dyeings will result, and the vat must be sprung with the bisulphite and zinc dust mixture above mentioned.

Lime is not to be added unnecessarily, and that introduced by the stock vat is sufficient to commence with. The alkalinity should be such that phenol-phthalein paper is just coloured pink, but frequent addition of the bisulphite-zinc mixture will necessitate sufficient addition of milk of lime to counteract any acidity, and to keep the vat in good order. It is preferable to spring with an alkaline mixture consisting of

10 parts bisulphite 57° Tw.,
1 part zinc dust,
2 1/2 parts milk of lime 20%.

The lime is added after the bisulphite and zinc dust have reacted, and the mixture used in quantities of 1—2 quarts as required.

After the vat has been replenished and sprung, it is thoroughly stirred and allowed to settle for half an hour.

It must be borne in mind that the wool takes up alkali from the vat, which may cause precipitation of indigo white. Should on this account additional lime become necessary, it must be carefully added in small portions, testing as already described with phenol-phthalein paper.

An excess of lime may be neutralised with dilute acetic acid, carefully checking the alkalinity with phenol-phthalein paper.

Dyeing is carried out as in the hydrosulphite-ammonia vat, and, owing to the lime present, the dyed goods must finally be soured and washed.

4. Indigo pure B.A.S.F./*R*.

Indigo pure B.A.S.F./*R*.

This brand, which is distinguished by the beautiful reddish tone of the shades dyed with its aid, possesses the same excellent fastness as the ordinary brands of Indigo pure, and is similarly dyed in the fermentation and hydrosulphite vats. Indigo R can be employed both for topping ordinary indigo or can be dyed in combination with it, and affords a convenient means of shading towards violet. It is of special interest as a substitute for the colouring matters which have been used for topping indigo dyeings to brighten the shade, and it is also useful for improving ordinary indigo dyeings, which for some reason have turned out duller than expected.

It is placed on the market as paste (Indigo pure B.A.S.F. paste 40 % R), as powder (Indigo pure B.A.S.F. powder R), and in a reduced form (Indigo solution B.A.S.F. 20 % R).

We recommend specially the solution applied in the hydrosulphite-ammonia vat; the paste and powder brands are suitable for the other hydrosulphite vats and for the fermentation vat.

To obtain the reddest possible shades with this brand, both the hydrosulphite and fermentation vats should be worked a little sharper than with the ordinary brands. The former vat must contain sufficient hydrosulphite to keep the liquor pure yellow and perfectly clear. Otherwise the treatment of the *R* brands is the same as that recommended for ordinary Indigo pure.

5. Treatment of Loose Wool.

Treatment of Loose Wool.

Various points relating to the treatment of loose wool have already been mentioned, so that it only remains to mention a few additional details of general interest.

To obtain good dyeings, it is very necessary that the wool be previously completely degreased, since greasy fibre cannot properly fix the dyestuff, so that in the after-processes much colour is lost, and the blue produced is insufficiently fast to rubbing. The scouring is usually performed by treatment with ammonia or soda at a temperature of 100—120° F., and carbonised material must have been previously passed through a bath of weak ammonia or soda. Wool which has been bottomed with acid dyes must also be neutralised before commencing to top with indigo, for, if any acid gets into the vat, the neutralisation of alkali caused thereby may lead to faulty dyeings.

It is advisable to wet out the wool before entering, as dry wool, especially in finer qualities, dyes unevenly, and also introduces such large quantities of air into the vat, as to affect the condition of the latter. The wool is wetted out with hot water and allowed to drain or hydro-extracted before it is entered into the vat. In the dyeing of fine wools small white lumps are sometimes formed; these are flocks of wool, which during the first dip do not dye well, or even refuse to take up any colour at all, and show up as white spots in the dyed material. When this tendency exists, it is well to wet out in a hot liquor containing ammonia, and to thoroughly squeeze the wool after dyeing. The manipulation of loose wool in dyeing has been described in the chapters dealing with the working of the fermentation and hydrosulphite vats. The quantity of wool which can be dyed at one time depends, of course, on the size of the perforated basket, and no more should be taken than can conveniently be worked; if the quantity is too large, the dyeing will suffer in evenness. About 65 lbs. is as much as should be dyed at one time in the hydrosulphite vat, because, as the wool is only gradually taken through the squeezers, the last portions of too large lots would be darker than the first portions, through having remained longer in the liquor.

In the methods of working, so far as discussed, the wool is dyed by moving it about in the vat liquor. We will now describe processes offering the advantage that stationary material is treated with dye liquor which is continually circulated through it.

Gruhne's Patent Dyeing Machine.

(German patent No. 108 225.)

Gruhne's Patent Dyeing Machine.

For this method of working the vat must be clear and free from sediment. Consequently, the fermentation vat is unsuitable, and only a hydrosulphite vat, preferably a hydrosulphite-ammonia vat prepared with our Indigo solution and Hydrosulphite conc. powder, can be recommended.

The apparatus (Fig. 12) may be regarded as a centrifugal dyeing machine. It consists of a perforated revolving drum *M*, a reservoir *K* for the dye liquor, and a pump *P*. During the circulation of the liquor the revolving drum, which serves to contain the wool, is kept in tight contact with the casing *T* by means of india-rubber rings *G*, and can be raised or lowered by means of the shaft *W*, which is worked through the bearing *L* by means of a lever *H* and a screw *S*. Within the drum *M* is a perforated tube *R*, which is suitably connected with the pipe R_1. By means of a three-way cock *H*, R_1 can be put into communication with either the pump *P* or the reservoir *K*. The pipe R_2 and the three-way cock H_2 connect the outer casing *T* either with the pump or the dye liquor reservoir.

The method of working is as follows:

The vat is set in the reservoir *K* and heated by means of steam to the desired temperature. The revolving drum *M* is evenly packed with dry loose wool and closed with the lid *D*. The wool is then freed from air by means of steam, which can pass through an opening in the lid. This renders unnecessary any previous wetting out of the wool. Through the condensation of the steam a vacuum is formed, so that the liquor is sucked up through the pipe R_2, and by regulating the cocks *H* and H_2 it is circulated through the material, either from the inside to the outside or in the reverse direction, as thought advisable. At the end of a quarter of an hour the pump is stopped, the pipe R_1 is unscrewed, and the liquor allowed to run into the reservoir through the cock H_2. The cylinder *M* is raised by means of the screw *S*, and set going as a hydro-extractor. The separated liquor runs through *R* into *K*. During hydro-extraction the indigo on the wool becomes oxidised, and another dip can then be given without re-packing the wool.

The vat is replenished with indigo solution (or stock vat) and sprung with hydrosulphite, when necessary, in the reservoir *K*. (See description of the working of the various kinds of vats.)

The advantages afforded by this method of dyeing are excellent penetration and, consequently, better fastness to rubbing, and the good condition, in which the material is left. The machine being closed, the air has but little access to the liquor,

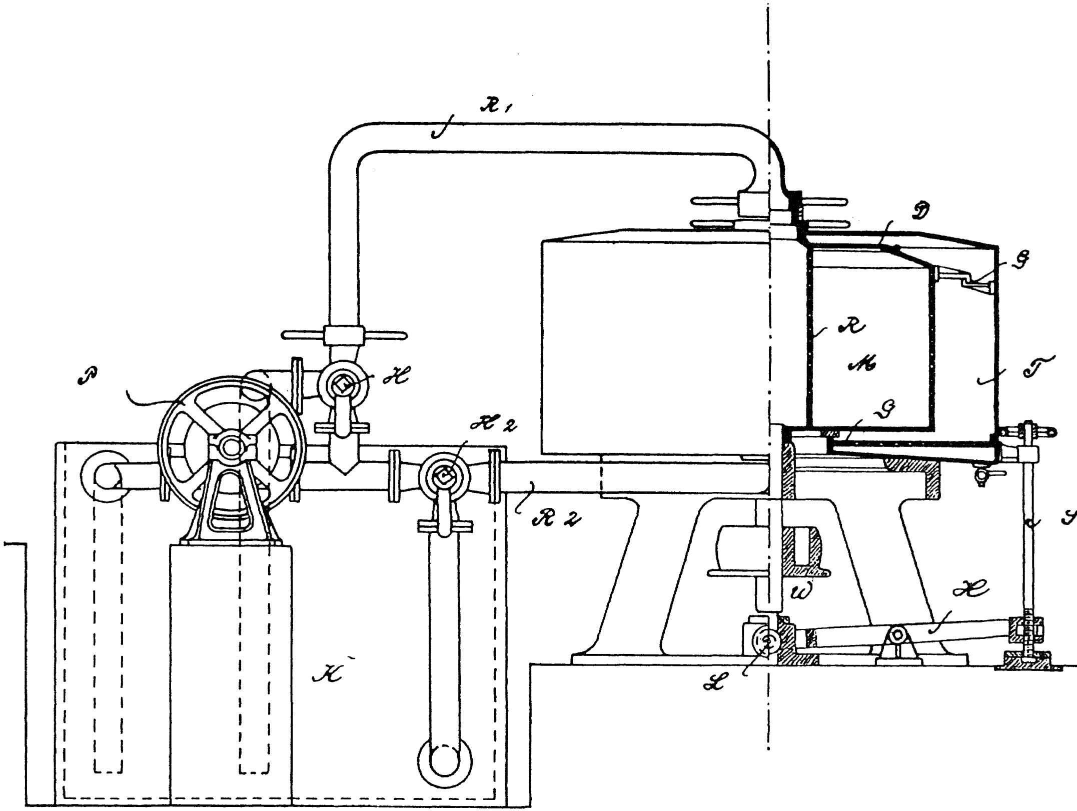


Fig. 12. Gruhne's Patent Dyeing Machine.

and hydrosulphite is thereby saved. The working capacity is good, lots of 45—55 lbs. can be dyed in one operation, and the rapid circulation of the liquor enables the duration of the dips to be shortened as compared with dyeing in an open vat. The indigo is utilised to the fullest extent, as all excess of liquor is removed by hydro-extracting.

This machine is supplied by Mess^rs. *C. G. Haubold jr.* of Chemnitz.

Treatment of the Dyed [illegible]

In addition to the points already mentioned in the general section, the following require to be borne in mind as regards the behaviour of dyed loose wool in the subsequent stages of manufacture.

The greasing or oiling of the wool for spinning does not as a rule affect the shade; medium and dark dyeings regain their original beauty on being scoured. Very pale shades, however, especially during warm weather, are sometimes dulled by the oil; this is presumably due to a partial destruction of the dyestuff, owing to the fermentation or decomposition of the oil. It is best avoided by keeping the oiled wool in a cool place, and not allowing it to remain too long in this condition.

In milling care must be taken to prevent overheating, otherwise the dyestuff is forcibly rubbed off the fibre, and the cloth appears spotted. Further, the water used for rinsing after milling must be as soft and free from lime as possible; if hard water be used, lime soaps will be precipitated on the wool and prevent the thorough washing out of the unfixed indigo, so that the cloth will not be fast to rubbing.

Carbonisation and decatising increase the brightness and the coppery tone of the shades without otherwise altering them.

6. The Dyeing of Slubbing.

Dyeing of Slubbing.

Slubbing is dyed in the ordinary open vat in the form of hanks, and also in special machines in bobbins.

Slubbing in Hanks.

For the former method both the hydrosulphite and fermentation vats can be employed. Hanks of about 1 lb. each are hung on cords, which are attached to a series of rods or poles, in such a way that the material is entirely immersed in the liquor. To prevent uneveness the hanks are turned during dyeing two or three times on the cords, and the relative position of the rods is changed, but any violent movement of the material must be avoided, or the wool will become felted. Oxidation is effected, in the case of the fermentation vat, by raising the rods from the vat by rope and pulley block, and allowing the hanks to drain; in the case of the hydrosulphite vat, each hank is taken out separately and immediately wrung by hand or passed through squeezing rollers.

Continuous Dyeing of Slubbing.

Slubbing is occasionally dyed continuously by passing it through the vat in the form of a band over a series of rollers, in a manner similar to that employed for the dyeing of cotton warps.

For this process, which allows of greater output and involves less handling than dyeing in the hank, we recommend the hydrosulphite-ammonia vat. The method of working is as follows: Several ropes of slubbing, separated from one another by pegs, are taken through a vat over a number of rollers, which are all under the surface of the liquor. After being in the vat a few minutes, the bands are passed through squeezing rollers and led over a large drum to oxidise. From hence they are led into the next vat, and so on. Before dyeing the slubbing is scoured and wetted out in warm water, to which ammonia has been added.

Slubbing in Bobbins.

The best results as regards the condition of the slubbing are, however, obtained by dyeing it in the form of bobbins ("balls"). For this purpose machines must be used, in which the dye liquor during circulation is as little as possible in contact with the air, and is kept at constant level. The removal from the balls after dyeing of superfluous liquor, and with it of unfixed indigo white, must be capable of being quickly effected, *i. e.,* before oxidation has taken place.

Obermaier's Revolver Machine.

For this purpose *Obermaier's* so-called "revolver" machine is usually employed. In this machine each ball is fixed horizontally in a separate cage, both ends of which are perforated. These cages are all connected at one end with a vertical cylinder, which is mounted in an open vat. By means of a pump the liquor is forced through the cylinder and balls. The cylinder with the ball carriers can be hoisted out of the liquor vessel by means of a pulley. Our hydrosulphite-ammonia vat is best suited for use with this machine, and is worked in the same manner as when dyeing loose wool. Since the liquor during circulation comes a good deal into contact with the air, hydrosulphite has to be added more frequently than to an ordinary vat. To obtain level dyeings, the balls must be wound uniformly and must entirely fill the cages.

The method of working is as follows: Having filled the cages with balls they are wetted out with hot water containing ammonia in a machine similar to the one used for dyeing. The cylinder and balls are then removed to another machine, in which the dye-vat is contained, and the liquor circulated for 20—30 minutes. To oxidise the dyestuff, either the cylinders are replaced in the wetting-out machine and water pumped through them, or the balls are removed from the cages and hydro-extracted.

Gruhne's machine, described on page 261, is also constructed in a special form (German patent No. 155388) suitable for dyeing slubbing.

7. The Dyeing of Woollen Yarn.

Dyeing of Woollen Yarn.

Woollen yarn can be dyed both in the hydrosulphite and fermentation [illegible]. We recommend the following method of working, using the hydrosulphite-ammonia vat (see page 250): For lots of about 50 lbs. a wooden beck, 10 ft. × $3^{1}/_{4}$ ft. × $3^{1}/_{4}$ ft. deep, will suffice. The wool, which has been well scoured with soda or ammonia and hydro-extracted, is entered into the vat on bent sticks, so as to be fully immersed in the liquor, and carefully turued under the surface. After $^{1}/_{2}$—$^{3}/_{4}$ hour the sticks are taken out one by one, and the yarn immediately wrung out and oxidised. The wringing can be performed by hand, or, preferably, with the wringing machine devised by *E. Geissler* in Cottbus (Fig. 13).

Geissler's Wringing Machine.

This machine consists of a framework mounted on wheels, so that it can be moved alongside any desired vat. The frame contains two india-rubber rollers; the front roller *A* can be pressed against the back roller *B* by means of a lever and weight. *B* is turned by means of cog-wheels, and the pulley *F* by a chain or belt connected with *B.* The chains *D,* which carry the sticks, run over the pulley *F.*

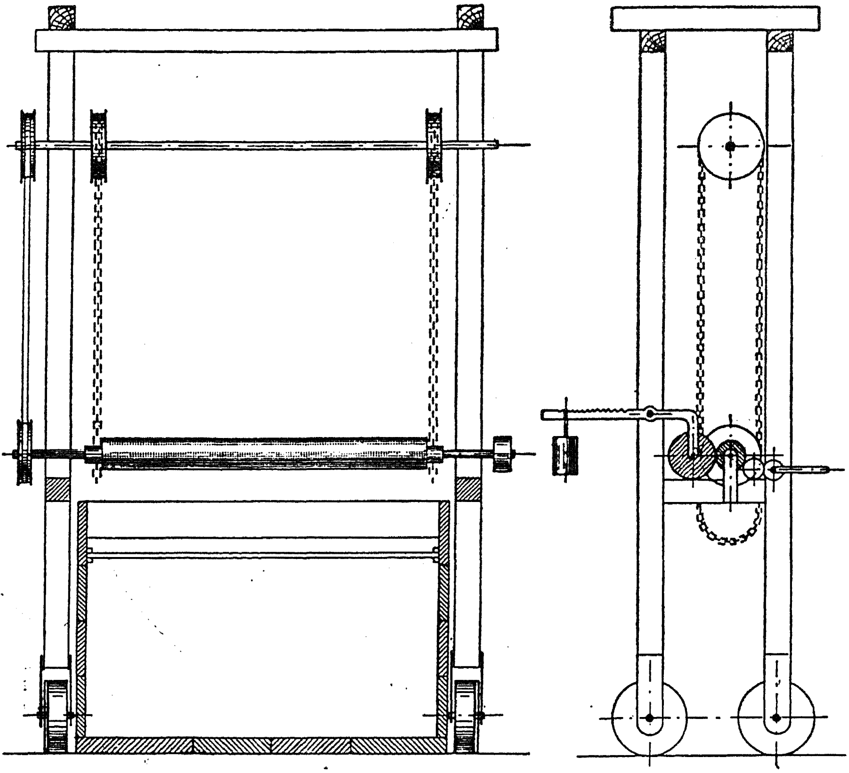


Fig. 13. Geissler's Wringing Machine for Yarn.

When the yarn is taken out of the vat it is wrung out a stick at a time; by means of the lever the rollers are separated, so that the stick can pass between. Each stick is hung on the chains *D* by means of hooks. The rollers are then brought together again and quickly turned by means of a winch. This wrings out the hanks, which are then carried upwards by the chain *D.* After having passed through the rollers, they are unhooked, and the next stick treated. That portion of the hank, which, on account of the stick, could not be squeezed, is wrung out by hand. The whole works smoothly and quickly; for wringing large lots four men are necessary. In this manner it is possible to dye 100 lbs. of worsted yarn sky blue in one operation, and the dyeing should be perfectly level, which is hardly possible without the use of a wringing machine.

The above machine is supplied by *Ernst Schulz* of Cottbus.

Medium and dark shades are best oxidised by allowing the wrung-out yarn to hang in the air, but light shades come out more level when oxidised in water. By adding acetic acid to the water the reddish tone can be increased, but the acid must, of course, be removed before another dip is given.

Gruhne's machine (page 261) can also be used for dyeing woollen hanks, which must be packed as evenly as possible. The method of working is the same as already described.

Dumons' Machine.

The dyeing of woollen yarn in the vat in the form of bobbins or cheeses is only very occasionally carried out. For this purpose *Dumons'* machine gives good results. In this machine the liquor can be circulated through the bobbins in either direction, so that even penetration is obtained. The vat is not exposed too much to the air, which is a great advantage in indigo dyeing machines.

8. The Dyeing of Piece-goods.

Dyeing of Piece-goods.

Piece-goods are dyed in the fermentation vat and in the various forms of the hydrosulphite vat. Of the latter we recommend the hydrosulphite-ammonia vat, worked with Indigo solution and Hydrosulphite conc. powder, on account of its numerous advantages already described. The vat is worked as when dyeing loose wool. The pieces are taken full width through the liquor either by hand or mechanical means. In the former case the cloth is kept continuously moving from one end of the vat to the other, always under the liquor, by means of iron hooks (hawking). In such vats as contain sediment (fermentation vat, bisulphite-zinc vat) a trammel net or wire sieve must be hung in the vat in order to prevent contact of the cloth with the sediment. Hawking by hand has many disadvantages, delicate materials may easily be injured by the hooks, and uneven dyeings or light places may be caused by air bubbles clinging to the pieces. Open-

Open-width Hawking Machines.

width hawking machines are simpler and more reliable in every respect, and can be used both with fermentation and hydrosulphite vats. A small machine worked by hand is shown in Fig. 14. It consists of a frame work, which is sunk in the vat in such a manner that the upper of the three wooden rollers is a few inches beneath the surface of the liquor. Several pieces are sewn together, and by turning the handle are, as in the jigger, alternately batched on one or the other of the bottom rollers, passing each time over the upper roller. The pieces must be loosely rolled, and must run smoothly and without folds. If heavy goods, difficult to penetrate, are being dyed, a pair of squeezing rollers may be substituted for the upper single roller.

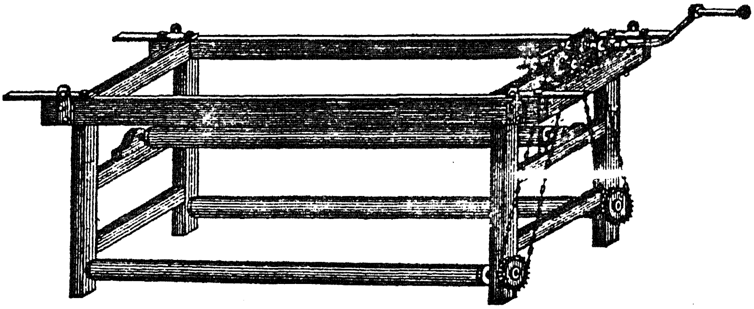


Fig. 14. Winch Hawking Machine.

For working on a large scale a modern, mechanically driven, open-width hawking machine is recommended.* Two such machines are shown, that in Fig. 15, being for use with hydrosulphite vats free from sediment, and that in Fig. 16 for fermentation vats or bisulphite-zinc-lime vats. The pieces are sewn together, an "end cloth" being attached, and the whole passes as an endless band under the liquor and through the squeezing rollers. Expanders prevent the formation of folds. A frequent passage through the squeezing rollers greatly assists the penetration (see page 40).

---

* These machines, as well as the open-width wringing machine to be described later, can be obtained from the firms of *H. Krantz,* Aix-la-Chapelle, *Lambert Schwarz,* Aix-la-Chapelle, and *Wagner & Hamburger,* Görlitz.

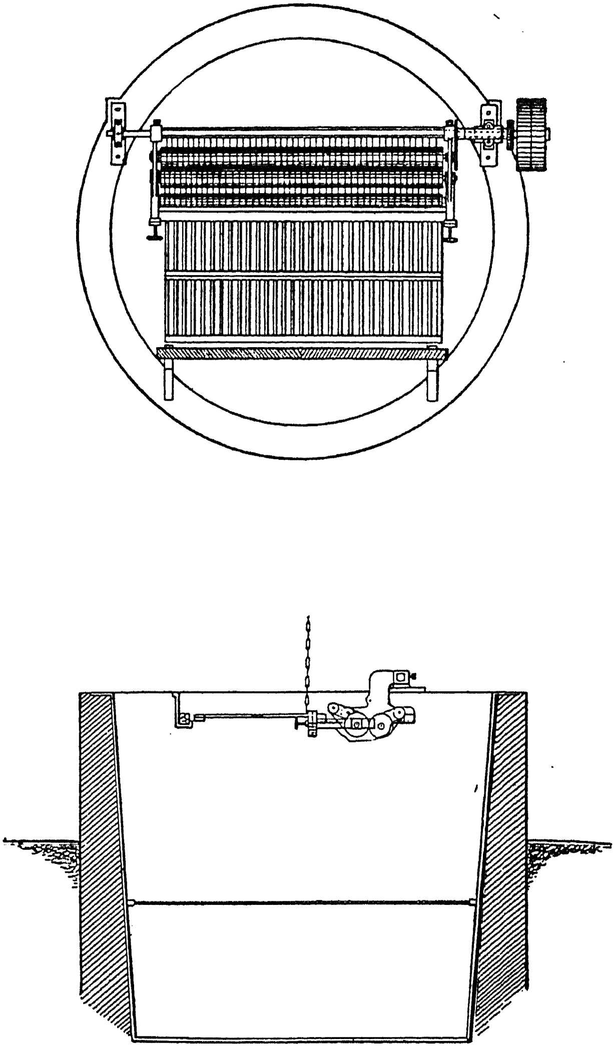


Fig. 16. Open-width Hawking Machine for Vats containing Sediment.

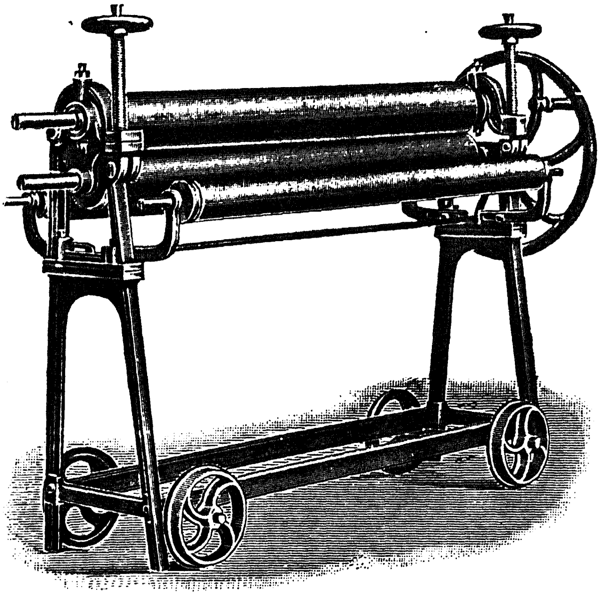


Fig. 17. Movable open-width Wringing Machine.

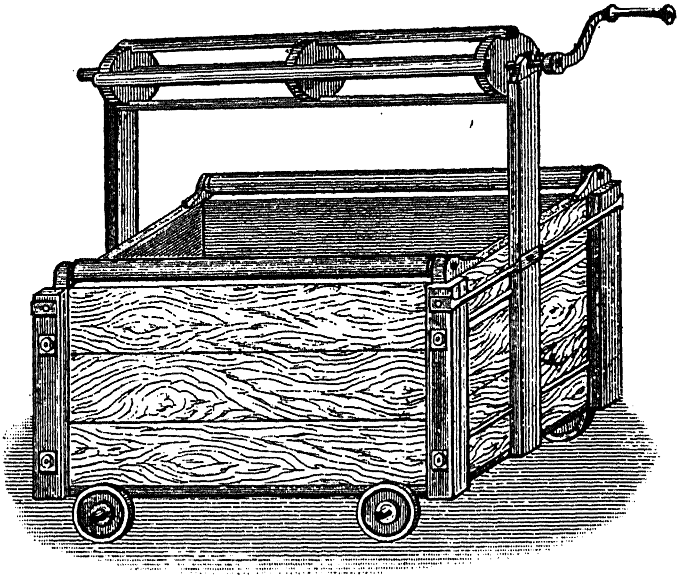


Fig. 18. Oxidising Trough.

After dyeing and before oxidation the pieces must be freed from excess of liquor, and, especially with the hydrosulphite vat, this must be effected immediately they leave the vat. A primitive method of removing the liquor, still sometimes practised, is to fold the material like a hank round two hooks placed on opposite sides of the vat. One of the hooks is stationary, while the other can be turned, and thus the cloth is wrung out. Another method, entirely out of date and bad for the cloth, is to pull it in rope form through a hole in a board. Both the above arrangements are only suitable for use with the fermentation vat, where complete and even removal of the liquor is not so essential. It is preferable in any case, however, and for the hydrosulphite vat indispensable, that the material be treated in the open width. For this purpose a travelling open-width wringer (Fig. 17), which can be moved from vat to vat, will be found suitable. The squeezing rollers are of iron covered with india-rubber.

To obtain the best results, it is absolutely necessary that the goods before dyeing be clean, and especially that they contain no oil from spinning. In order that this may be the case, it is important that the spinner should only employ easily saponifiable oils, which are removed without difficulty by scouring. Spotted dyeings and inferior fastness to rubbing can often be traced to the presence on the cloth of residues of low quality difficultly saponifiable spinning oils. Should the goods contain much oil, which can be recognised by the smell, they must be scoured lukewarm with soda (1—2 % of the weight of the material) and then rinsed with water as soft as possible to remove the saponified grease. If the rinsing water is hard, it must be previously treated with a little soda, otherwise lime soaps may be precipitated on the goods, giving rise to irregular dyeings not fast to rubbing. Milled cloths are freed from oil and soap by rinsing lukewarm with dilute ammonia (1 gallon per 500 gallons water).

Before entering the vat, the goods must be wetted out and hydro-extracted or squeezed, after which they should not be allowed to lie on a trestle, or the moisture in the piece may become unevenly distributed, and unlevel shades result. Carbonised goods are to be previously freed from acid, which would otherwise neutralise the alkali necessarily present in the vat.

The duration of a dip is, as a rule, about half an hour, but if thick, heavy goods are to be thoroughly penetrated, dips of one to two hours may be given. In dyeing light shades, the vat, whether fermentation or hydrosulphite, should be quite weak and the dips long, if level results are to be obtained. The hydrosulphite-ammonia vat is, in this case, to be kept distinctly alkaline, so that the indigo white may be taken up gradually and evenly.

The goods are oxidised by being pulled over a bar (Fig. 18) or run through cold water. The latter is specially recommended in the case of light shades, as oxidation is slow and even.

A thorough washing follows for the removal of unfixed dyestuff and to prevent rubbing off. The pieces are rinsed either in rope form or open width, then washed with fuller's earth, and again rinsed with water.

9. Improvement of Defective Dyeings.

Improvement of Defective Dyeings.

One of the most common faults incidental to indigo dyeing is the rubbing off of the colour. This is due to unfixed indigo, and indicates that the dyed material has been insufficiently washed off, or that some mistake has been made in dyeing or milling. The only remedy consists in washing the cloth with fuller's earth until all the loosely attached dyestuff is removed. If the goods are then too light, they must be re-dyed.

The problem often presents itself, how to increase the brightness of dyeings, which have come up too dull. This can sometimes be done by steaming the cloth, or by passing it through hot water, to which 1 gallon of acetic acid per 100 gallons has been added. Either treatment increases the reddish cast or coppery tone of the dyeing. In mixture cloths made from a blend of blue and white wool, the dullness may be caused by the "white" wool being yellowish in tone. The yellow tinge may be removed by bleaching with hydrogen peroxide. 1—2 parts of commercial peroxide are added to 8 parts of cold water, and the solution made faintly alkaline with caustic soda. The wetted-out and hydro-extracted cloth is left in this bath for two hours, and turned from time to time by means of a winch, then taken out allowed to lie piled up for six hours, washed in cold water, to which a little bisulphite has been added, rinsed in clean water, and dried.

Uneven dyeings, caused in the case of wool dyed material by spots due to milling or rubbing, or in piece dyed goods by some mishap to the hawking machine, can only be put right by taking them through a "blank" vat. To every 100 gallons water at 120 ⁰ F. add $^1/_4$ lb. Hydrosulphite conc. powder and $^1/_2$ pint ammonia. Phenol-phthalein paper should be just slightly coloured red by the bath. Treat the well wetted-out and hydro-extracted pieces for about an hour in the above vat on the open-width hawking machine, pass through squeezing rollers, also in the open width, and rinse. We would remark, however, that in such cases a levelling up is only possible if the difference between the shade of the spots and the desired shade is not too great. The treatment can also only be undertaken when the piece has no white selvedges, as the latter would be stained.

Pieces, which are too dark, can be made lighter to a certain extent by treatment with potassium permanganate, which destroys indigo on the fibre. The manganese dioxide thus deposited is then removed by means of oxalic acid. An ordinary winch piece dyeing or washing machine may be employed, the concentration of the stripping bath and duration of treatment being regulated according to the desired effect. The following example will give an idea of the procedure: For 2 pieces of 50 lbs. each dissolve $^3/_4$ lb. potassium permanganate in 350 gallons cold water and add 2 quarts sulphuric acid 168 ⁰ Tw., well wet out the pieces, and work them in the cold bath for 1 hour. Rinse with water and work for $^1/_2$ hour in a bath containing 1 lb. oxalic acid per 40 gallons water at 120 ⁰ F. Then rinse well. A pattern may be taken, if necessary, during the permanganate treatment and put through an oxalic acid bath to ascertain the extent of the stripping action.

10. The Tinting or "Blueing" of Wool in the Vat.

Tinting of Wool in the Vat.

This process, first proposed by *F. V. Kallab,* consists in simultaneously bleaching the wool by means of hydrosulphite or hydrosulphurous acid, and tinting it with indigo, and is founded on the fact that indigo white can be sufficiently well fixed on the fibre, even in acid solution. The bleaching bath is to be regarded as a weak acid vat containing an excess of hydrosulphite.

Loose wool, slubbing, or yarn can be treated in this way. Indigo solution B.A.S.F. 20 $^0/_0$ or Indigo vat B.A.S.F. 60 $^0/_0$ are most suitable for the purpose, but a stock vat set according to the recipe on page 255 may also be employed.

Recipe for the bleaching bath.

To every 500 gallons water at 120^0 F. add $2^1/_2$ lbs. Hydrosulphite conc. powder, $^1/_2$—1 oz. of Indigo solution 20 $^0/_0$, or a corresponding quantity of Indigo vat 60 $^0/_0$, or of the stock vat, and 1—2 gallons bisulphite 77^0 Tw. Enter the well wetted-out and hydro-extracted material, leave in the bath for $^1/_2$ hour with an occasional turn, squeeze or wring out, rinse and dry, avoiding too high a temperature. The bleaching is best performed in a clean wooden beck. The shades obtained in copper vessels are less bright.

11. The Dyeing of Unions.

Dyeing of Unions.

Unions are but seldom dyed with indigo, and then only in the case of special forms of piece-goods. Loose material of mixed cotton and wool, intended for subsequent milling, cannot be satisfactorily dyed entirely in the vat. The only possible way would be to first dye the wool in a normal warm wool vat, and then cover the cotton in a cold wool vat, but the cotton would lose too much in milling. For covering both fibres equally, a cotton dyestuff, sufficiently fast to milling, must be used in conjunction with indigo.

On account of the sensitiveness of wool to alkali, unions must not be dyed in cotton vats with the exception of the cold fermentation vat. In this vat, used in China and other oriental countries, which is worked comparatively weak in alkali on account of the sensitive character of the fermentation process, cotton, wool, and silk may be dyed. If, on the other hand, a normal warm wool vat be employed, the wool is dyed much deeper than the cotton, and the two fibres can only be simultaneously dyed an equal depth of shade from a cold wool vat or one at 90—100° F. For example, a soda vat for wool (page 231) or a potash vat for cotton (page 98) may be used. After setting or replenishing these vats in the usual manner warm, they are allowed to cool, and the union material is then entered. Any hydrosulphite vat described in previous sections can also be employed when used cold, less hydrosulphite being necessary than when worked warm. For this reason and because an excess of hydrosulphite prevents the dyestuff from going on to the cotton fibre, a hydrosulphite vat for unions must contain less reducing agent than a warm wool vat. For further particulars we refer to the detailed description of the various vats already given.

12. The Dyeing of Silk.

Dyeing of Silk.

Although silk, like wool, is sensitive to alkali, it is distinguished from the latter by being easily dyed in a cold vat. For dyeing silk both cold and warm wool vats and cold cotton vats may be employed, provided that the amount of alkali in the latter is somewhat reduced. Both the ordinary brands of Indigo pure and the *R* and *G* brands are suitable.

In oriental countries considerable quantities of silk are dyed with indigo in the cold or moderately warm fermentation vats as used for cotton, but in Europe the dyestuff finds little application for this purpose, and then only for the production of white effects on a dyed ground. The patterns are printed by means of a resin or wax resist, as the ordinary cotton resists containing copper or lead salts are not sufficiently protective. The resisted material cannot be dyed in a warm vat, as the wax, etc. would melt and run. The use of warm vats is, therefore, confined to silk yarn and the production of self shades on piece-goods. The fermentation vat yields greenish shades with plenty of body, whilst the shades produced in other vats are redder and, if dark, of a more coppery hue. For dyeing warm, *i. e.,* for goods not printed with a resist, we recommend either the soda vat (page 231) or the hydrosulphite-ammonia vat (page 250) prepared with our Indigo solution 20 % and Hydrosulphite conc. B. A. S. F. powder, or if the dyer prefers to prepare his own stock vat, the bisulphite-zinc-lime vat (page 257). The setting, concentration, and working of these vats is the same as for wool dyeing. For dyeing in the cold the hydrosulphite-ammonia or zinc-lime-bisulphite vats may be used, and are worked as in wool dyeing, the difference in temperature excepted; the stock vat for the zinc-bisulphite-lime vat is, of course, prepared warm. The dips last for about 30 minutes, and the material is finally rinsed with dilute acetic acid (1/4 gallon acid 10° Tw. to 100 gallons water), and dried at a moderate temperature.

The zinc-lime vat is also suitable, and is set as for cotton, except that about one quarter as much lime is taken. For a dye-vat of 200 gallons, for example, there is first prepared a

Stock vat.

Take

12 1/2	lbs.	Indigo pure paste 20 % SB or a corresponding quantity of another S brand, mix with
1 3/4	»	zinc dust stirred up with 5 gallons hot water (120—140° F.),
2 1/2	»	quicklime, which is added in the form of a freshly slaked, even, and warm paste.

Dilute with hot water (120—140° F.) to 10 gallons, stirring occasionally. In about 5 hours the mixture should be pure yellow and ready for adding to the dye-vat.

Preparation of the dye-vat.

To the cold water contained in a wooden or metal vessel add 1/2 lb. zinc dust and 1/2 lb. quicklime slaked to a paste. After standing a few hours, add the stock vat and, as soon as the sediment has settled, commence dyeing.

It is a feature of the zinc-lime vat that the hydrogen evolved by the action of the unaltered zinc dust and lime in the sediment tends for some time after the vat has been set to force the sediment up to the top. In order to prevent this occurring during dyeing, and so soiling the goods, it is necessary to well rake up the vat before commencing work, so that gas enclosed in the sediment may escape, and then allow the sediment to settle again.

The vat liquor as well as the sediment should always be yellow. If, through continued dyeing, it becomes green, it must be "sprung." The quantities of reducing agent required for this purpose cannot be definitely stated, but for a vat of 250 gallons 1/2—1 lb. zinc dust added at the end of a day's work will usually suffice.

The vat should not become too cold in winter, a temperature of 70—75° F. (as in summer) should be maintained.

The goods are hung on a dipping frame and dyed in dips of 10—20 minutes. A dark shade requires 6—8 dips. As previously mentioned, the dyed goods are soured with dilute acetic acid, and dried.

The following resist is suitable for the production of white effects:

Take 50 parts resin,
7 1/2 » turpentine,
30 » tallow,
10 » wax,

and melt together on the water bath to a homogenous mass. Print from a furnishing pad heated by means of steam.

After dyeing in one of the cold vats described above, the material is soured, dried, and the resist removed with benzine.

1805

INDEX.

Page

After-treatment, process for — in yarn dyeing 56
Albumen colours, combination with indigo printing 153
Alkali in the printing colour ... 135
Alkali in the vat ... 38, 41, 226, 245
Alkaline gum thickening and starch thickening 134, 138
Alizarine colours, printing of — along with indigo 154
Alizarine Red, discharges on — with indigo 160
Ammonia-hydrosulphite vat for wool 245, 250
Ammonium chloride in the vat ... 254
Ammonium chloride vat see hydrosulphite-ammonia vat.
Analysis of indigo 10
Analysis by dyeing tests 11
Analysis by means of hydrosulphite 14
Analysis by means of permanganate 21
Analysis, colorimetric 11
Analysis methods 12
Analysis, gravimetric — by the vat method 27
Aniline colours, coloured discharges with indigo on — 159
Aniline colours, printing of — along with indigo 151
Aniline colours, topping of indigo with — 58
Aniline Black in combination with indigo 153, 181, 200, 220
Animal fibres, printing of — ... 150
Azo colours, coloured discharges with — 170
Azo colours, indigo discharge prints on — 159
Azo resists 199, 216

Bacteria see vat-bacteria.
Bancroft 124, 126
Bandana process 190

Page

Battik printing 192
Bastard vat 232
Bengal indigo 31
Bimlipatam 31
Binz ... 13, 18, 28, 32, 34, 38, 41, 76, 87, 167, 228
Bisulphite-zinc-lime vat for cotton 93
Bisulphite-zinc-soda vat for cotton 91
Bisulphite-zinc-lime vat for wool 257
Blackish shades on cotton ... 56, 67
Bleaching bath with indigo for wool 272
Blue Print 197
Blueing of wool; see tinting ... 272
Bran vat 99
Bran sack 238
Bromate discharge 185
Bromate discharge for Alizarine Red on indigo 189
Bromindigo see *R* brands.
Bromindigo, behaviour of — to chromate discharge 173
Bronze printing 115
Brushed Blue 124
Brylinski see Scheurer.

Cabiati's process 201
Calculation of cost of an indigo dyeing 100
Calendering, influence of — on the shade 60
Carbonising 269
Carbonised wool, dyeing of — ... 261
Cheese Dyeing 72
Chemically pure indigo 15
Chibori process 190
Chinese vat 98
Chloranisidine resist 217
Chlorate discharge 183
Chlorate-prussiate discharge ... 185
Cold fermentation vats see fermentation vats.

Page

Colloidal indigo 6, 109
Colorimetric methods of analysis 11
Coloured discharges on indigo ... 170
Coloured discharges with indigo on Aniline and Alizarine colours 159
Coloured resists 198
Coloured resists for indigo printing 156
Coloured discharges, production of — 170, 186
Comparative dyeings 11, 243
Continuous vat 62
Continuous vat, resists for — ... 221
Cop dyeing 72
Copper, preparation with — ... 52
Copperas vat... 79
Coppery shades on cotton 52
Coppery shades on wool 249, 263, 270
Cost of indigo dyeing; see calculation.
Cotton dyeing 49
Cotton piece dyeing 60
Cotton piece dyeing on one side 61
Cotton vats 76
Cotton yarn dyeing 50
Cotton yarn dyeing, after-treatment in — 56
Cotton yarn dyeing, preparation in — 56
Cream resist 199, 216
Crease formation, prevention of — 64

Decatising indigo dyeings 263
Derivative of indigo; see *R* and *G* brands and Bromindigo
Destruction of indigo in the vat 96, 240
Detection of indigo on the fibre 50
Dextrine in indigo printing ... 145
Dextrine thickening 164
Diastafor for indigo printing ... 144
Dip in the vat 38
Dipping frame 61
Dipping vat 60
Discharge printing with indigo on basic colours 159
Discharge printing with indigo on Alizarine colours 159
Discharge printing with indigo on azo colours 161, 165
Discharge printing on indigo ... 166
Discharge resists 201, 212
Discharge resist for Aniline Black on indigo 183

Page

Discharge resist under steam indigo blue 156
Double style 158, 176
Dumons' machine 267

Elbers' coloured discharge process 170
Elbers' indigo grey 120
Estimation of indigo on the fibre 32
Evenness of cotton dyeings 50, 51
Evenness of cotton piece dyeings 65
Evenness of wool dyeings ... 245, 266
Export statistics for indigo 7
Extraction of indigo from the fibre 32

Fastness of indigo dyeings 44, 141, 225
Fastness, increasing the — of indigo on cotton 59
Fastness to chlorine of indigo dyeings 41, 45
Fastness to light of indigo dyeings 45
Fastness to rubbing of indigo dyeings 41, 45
Fastness, poor — to rubbing of indigo dyeings on cloth; see rubbing off.
Faulty dyeings, improvement of — 270
Fayence blue 125
Fermentation vats for cotton 53, 95
Fermentation vats, cold 100
Fermentation vats for wool 227, 231
Fermentation vats for wool, construction of — 229
Ferrocyanide of potassium see prussiate.
Finish for resist prints 204
Finishing, influence of — on the shade 56
Fixation of indigo by glue 68
Formaldehyde indigo white 113
Formaldehyde-sulphoxylate for indigo printing 146
Fuller's earth 270

G brand of Indigo pure B. A. S. F. 8 45, 56, 66, 152, 186
G brand of Indigo pure B. A. S. F., behaviour of — in the discharge 173
Geissler's wringing machine ... 265

Page

Glacial acetic acid method of analysis 32
Glass plate test 88, 255
Glucose printing process 126
Glucose printing process, directions for carrying out the — ... 130
Glue, addition of — to the vat (cotton) 69
Glue in the hydrosulphite vat (wool) 246
Glue preparation, influence of on the dyeing 44, 69
Grämiger cop dyeing machine ... 74
Grape sugar printing process; see glucose.
Grape sugar, preparation with — in indigo printing 131
Gravimetric analysis 27
Grey with indigo, Elbers' process 120
Grounding with Aniline colours and Kryogene Black 58
Gruhne's dyeing machine ... 261, 267
Guinea styles 60
Gum thickening, alkaline ... 135, 139

Half-linen 105
Half-resists 157
Hawking machine 268
Honey vat 128, 228
Hydrosulphite conc. B. A. S. F. powder 64, 84, 245
Hydrosulphite-ammonia vat for wool 245, 250
Hydrosulphite analysis and indigo red 21
Hydrosulphite-lime vat for cotton; see bisulphite-zinc-lime vat.
Hydrosulphite-lime vat for wool 258
Hydrosulphite methods of analysis 14
Hydrosulphite-soda vat for cotton 84
Hydrosulphite-soda vat for wool 254
Hydrosulphite solution, production of — 85
Hydrosulphite solution, testing of — 85
Hydrosulphite vats for wool ... 244

Indanthrene printed along with indigo 152
Indian print 194
Indigo brown 8, 28
Indigo gluten 8

Page

Indigo derivatives; see *R* and *G* brands.
Indigo odour; see vat odour.
Indigo red 8
Indigo red. behaviour of — in the vat 42
Indigo red. estimation of — in presence of indigo 20
Indigo red and hydrosulphite analysis 20
Indigo red and permanganate analysis 26
Indigo solution B. A. S. F. 37, 86, 97, 245, 246
Indigo solution B. A. S. F. 20 % for fermentation vats 241
Indigo statistics 7
Indigo sulphate 14, 15
Indigo vat B. A. S. F. ... 38, 97, 246
Indigo white (see also Indigo vat and Indigo solution) 28, 35, 37, 39, 42, 70, 236, 245, 256, 274
Iron, grounding cotton with — 57, 68
Iron, topping with — 57, 68

Japanese resist processes ... 190, 195
Japanese vat 98
Java indigo 8, 31
Jute 105

Kallab 272
Köchlin's discharge process 170, 172, 174
Krantz machine for cops and cheeses 74
Kryogene Black as ground for indigo 58
Kurz and Kunert's discharge process 171

Lactic acid resist 157
Lapis style 183, 199
Leese's printing process 129
Lime soaps 263, 269
Linen 105
Loose cotton 75
Loose wool 225, 260
Loose wool, machine for dyeing — 261
Losses in rinsing 101, 249
Losses in the vat 28, 78, 80, 87, 91, 101, 240, 257
L powder, production of paste from — 82
Lurati's process 200

Page

Maltose printing process ... ... [illegible]
Manganese brown, employment of — in printing ... ... [illegible]
Mercer's discharge process ... ... [illegible]
Mercerisation, influence of — on the dyeing ... ... 66, [illegible]
Mercerisation, partial — ... ... [illegible]
Metanitraniline resist ... ... [illegible]
Mexican indigo ... ... [illegible]
Mild condition of wool vats ... [illegible]
Milling, influence of — ... ... [illegible]
Milling spots .. .. [illegible]
Molasses vat ... ... [illegible]

α-**N**aphthylamine Claret, coloured discharge with — ... ... [illegible]
Natural indigo: see plant indigo.
Nitrosamine Red discharge on indigo [illegible]
Nitrosamine Red resist ... ... [illegible]
Normal indigo for analysis 14
Normal indigo solution 18

Obermaier machine 76, 264
Odour of indigo; see vat odour.
Oil colour printing 115
Olive resist 211
Open-width hawking machine (wool) 268
Open-width wringing machine ... 269
Orange resist 210, 218
Orange resist with azo colours ... 218
Orpiment 35
Orpiment vat 123
Oudh 31
Over-reduction (see also losses in the vat) 166
Over-sharpening of fermentation vats 238
Oxidation 38, 40, 142, 270
Oxidation discharges (see also chlorate and chromate discharges) 168

Painted Blue 124
Paranitraniline Red resist 217
Para Red, coloured discharge with indigo on — 161, 165
Para Red combined with indigo printing 154
Paste from Indigo pure B.A.S.F./*SL*, preparation of — 230

Page

Paste from Indigo pure B.A.S.F./*L* powder, preparation of — ... 82
Penetration (cotton) ... 40, 50, 91
Penetration (wool) ... 40, 268, 269
Permanganate, analysis by — ... 21
Permanganate analysis and indigo red 26
Perrotine 205
Phenol-phthalein paper, use in indigo dyeing 90, 97, 234, 238, 253, 256
Piece dyeing (cotton) 59
Piece dyeing (wool) 267
Pieces, improvement of defective — 270
Pieces (cotton), penetration by dyeing warm 50
Pink resist 219
Planella, machine for cotton yarn 54
Plant indigo and Indigo pure 7, 41, 242
Plant indigo, production of — ... 8
Plant indigo, impurities in — 8, 42, 43
Plant indigo statistics 7, 8
Plate test 50
Potash vat 98
Powder brands, Indigo pure B.A.S.F., making of pastes with — 82, 230
Preparation of piece-goods before dyeing, methods of — ... 57
Preparation of yarn before dyeing, methods of 56
Printing colour for indigo (glucose) 139
Printing colour for indigo (Rongalite) 148
Printing, general remarks upon — 109
Printing methods, classification of — 112
Printing methods, development of — 123
Printing methods with Rongalite 146
Printing methods for wool and silk 151
Prud'homme 124
Prussiate discharge 183
Prussian Blue resist 201, 215

Rawson's method of analysis 13, 28
R brands of Indigo pure B.A.S.F. 9 44, 56, 66, 151, 173, 186
RBN brand of Indigo pure B.A.S.F. 9
Reactions on the fibre; see detection.
Reactions in the fermentation vat 236
Realgar; see orpiment.
Recovery of waste indigo; see waste indigo.
Reducing agents 35

Page

Reducing agents, influence of — on the dyeing 39

Reduction discharges 167

Red resist 216

Reddish tone of dyeings 43, 52, 251

Refined indigo 26, 29

Regordosa, machine for cotton yarn 54

Resin resist 195, 275

Resists, action of 198

Resists, coloured 198

Resists for continuous vat 221

Resists for silk 275

Resist printing 190, 202

Resist printed goods, dyeing of — 204

Revolving dyeing machine Krantz 74

Revolving dyeing machine Obermaier 264

Ribbert's printing process 130

Ribbert's resist process 157

Roller machine for resist printing 208

Rongalite printing process ... 126, 146, 161, 164

Roulette or roller vat 62

Roulette or roller vat, resist for — 221

Rubbing off of pieces 270

Rung; see Binz.

Running away of wool vats ... 240

Sarong 193

S brands of Indigo pure B.A.S.F. 37

SL powder, production of a paste with — 83, 231

Schaab's resist process 221

Scheurer and Brylinski 32

Schlieper's printing process (Schlieper & Baum) ... 130, 131

Schumacher 200

Schützenberger 124, 244

Schwartzenberg and Schwartz 8, 42

Shade, coppery — on cotton ... 52

Shade, blackening of — by sizing 56, 68

Shade, improvement of — (wool) 270

Shade, influence of dyeing on — (cotton) 82, 87, 90

Shade, influence of dyeing on (wool) 236, 253, 256

Shade, influence of glue preparation on — 68

Shade of indigo dyeings 43, 226, 249

Sharp condition of vats ... 90, 233

Page

Sharpening 79, 90, 233, 236, 237, 259

Sharpening excessively ... 236, 238, 240

Silk, printing indigo on — 151

Silk, dyeing indigo on — 273

Silk, discharging indigo on — . . 175

Silk, resisting indigo on — 195, 274, 275

Sizing of cotton dyeings ... 56, 67

Slendang 192

Sliver 75

Slubbing 263

Smell of indigo; see vat odour.

Soda vat 231

Solid blue 124

Souring of dyed goods ... 52, 65

Souring baths for discharge printing 213, 217

Souring baths for resists 181

Souring baths, recovery of indigo from —; see waste indigo.

Spencer system for cotton yarn ... 54

Spinning capabilities of cotton ... 75

Spinning capabilities of wool 248, 260

Spinning oil 263, 269

Spots on cotton pieces 62, 65

Spots due to rubbing 271

Squeezing rollers ... 63, 246, 250, 269

Standard for analysis 15

Starching of pieces 67, 202

Starch thickening, alkaline . . 134, 138

Steam discharge pastes 186

Steaming in indigo printing 127, 141

Stencil resists 195

Stock vat 77, 78, 255

Streaky dyeings 50, 65, 90

Striped or spotted yarn 50

Striped or spotted pieces 267

Stripping of indigo from wool ... 271

Sublimation, printing of indigo by 120

Sugar vat 126

Suint vat 240

Sulphonation of indigo for analysis 17

Sulphoxylate; see Rongalite.

Sulphide of arsenic; see orpiment.

Sulphur colours, printing along with indigo 153

Sulphur colours as ground for indigo; see Kryogene Black.

Sulphur, production of designs with — 119

Sulphur resist in indigo printing 156, 158

Page

Tagliani 118, 157
Tannin discharge style with indigo 159
Tendering of the fibre in chromate discharge 174
Testing of indigo dyeing 50
Thiazine Red resist; see pink resist.
Thickening (see also gum and starch thickening) 176, 177
Thickening for indigo printing 134, 138
Thies' cop dyeing machine 74
Thompson's discharge process ... 169
Tin crystals discharge 167
Tin as a reducing agent ... 36, 124
Tinting of wool in the vat 272
Titrimetrical estimation of indigo by hydrosulphite 14
Titrimetrical estimation of indigo by permanganate 21
Tjanting 192
Tolyl indigo; see *G* brand.
Tops (slubbing) 263
Trammel 267
Treatment with glue; see glue preparation.
Tschaps 192
Tulleken 10, 42
Turkey red, discharge on — 161, 163
Turkey red, printing of — along with indigo 155
Tying, resist by — 190

Ullgren 28
Uneven dyeings 50, 61, 270
Uneven pieces, improvement of — 271
Unions 272
Urine vat 96
Utilisation of indigo in the vat (see also under losses and destruction 29, 34

Vat-bacteria 228, 237
Vat-dip 35, 38
Vat dyeing, general remarks upon — 38
Vat, fermentation — 36, 227
Vat, general remarks upon the — 34

Page

Vat, method of analysis 28
Vat odour 57, 95
Vat recipes (fermentation vats) ... 231
Vegetable fibres, dyeing of — ... 49
Vegetable indigo; see plant indigo.
Völker 126

Ward's printing process 127
Warm vats; see fermentation vats.
Warp dyeing 54
Waste indigo, recovery of — ... 102
Wax resists 192, 275
Wetting-out vat 63, 203
Wetting-out rollers 63
White discharges 176, 188
White tips on wool 245
Wilhelm 145
Winch hawking machine 268
Woad 228
Woad vat 233
Wool, discharges on — 175
Wool dyeing 225
Wool dyeing machine 261
Wool, influence of the quality of the — on dyeing 260
Wool printing with indigo 150
Wool, Scouring of — 260
Wool, treatment of — in dyeing 260
Woollen piece dyeing 267
Woollen yarn dyeing 265
Wringing machine for pieces .. 269
Wringing machine for yarn ... 266

Yarn dyeing 50
Yarn dyeing, mechanical appliances for — 54
Yarn dyeing (woollen) 265
Yellow resists 202, 211

Zinc dust discharge 167
Zinc-lime vat (cotton) 76
Zinc-lime vat (silk) 274